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X-RAY SPECTROCHEMICAL ANALYSIS

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Qualitative and quantitative spectrochemical analysis, using the emission spectra of elements in the optical wavelength region, has been successfully applied since the days of Bunsen and Kirchhoff. In the past decade a basically similar method of analysis, using the emission spectra in the X-ray wavelength region, usually excited by way of fluorescence, has been introduced into laboratory practice. This method, which of course employs completely different techniques, has already proved very useful in a large variety of cases.

The specific character of the spectrum of the light emitted by each chemical element when heated or burned, has been put to use for the identification of elements for nearly a century. To-day this method ranks among the most sensitive means for the detection of minute traces of impurities. Techniques have been established which make it an easy and fairly accurate method of *quantitative* chemical analysis, supplementing and sometimes supplanting classical wet chemical methods ¹⁾.

The optical spectra of most elements are very complicated: they usually contain hundreds or even thousands of lines (*fig. 1a*). Although this is not a limitation in principle, the usefulness of spectrochemical analysis is often limited in practice by difficulties in the identification of components in a mixture when the spectrum is very crowded. Other limitations of the method will be mentioned at the end of this article.

In the past decade another method of spectrochemical analysis, based on the X-ray instead of the optical spectra emitted by the elements, has acquired considerable importance. This method has similar characteristics to those of the optical method and it has additional features, e.g. that of being non-destructive — certainly an important asset for

some cases. An essential advantage, however, as compared with the optical method, is the great simplicity of X-ray spectra (*fig. 1b*). It would perhaps seem that such an advantage — which is of a practical nature — would be completely out-

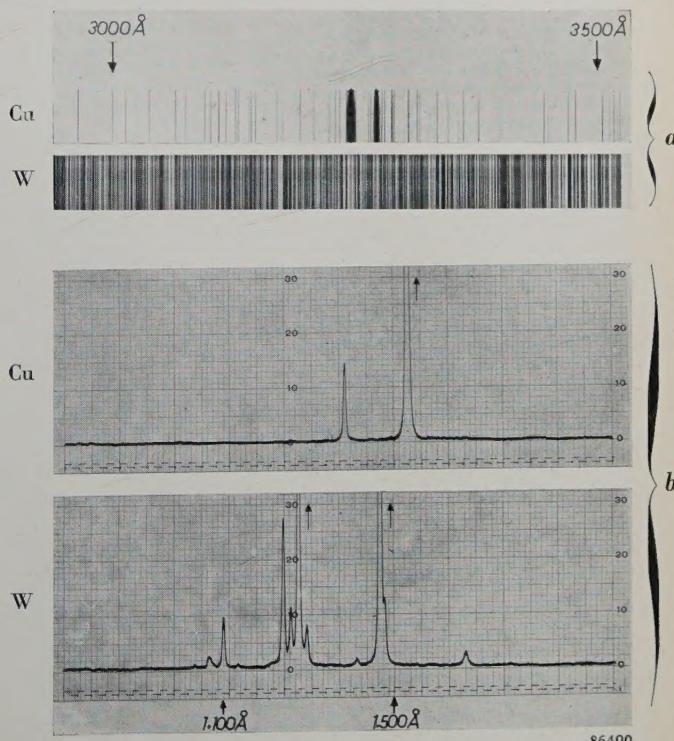


Fig. 1. a) Optical spectra of copper and tungsten in the region 3000 to 3500 angstroms. b) X-ray spectra of same elements.

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¹⁾ See, for example, N.H. Nachtrieb, Principles and practice of spectrochemical analysis, McGraw-Hill, New York 1954; N. W. H. Addink and W. de Groot, Spectrochemical analysis, Philips tech. Rev. 12, 337-348, 1950/1951.

weighed by the more complicated technique involved in handling X-rays instead of light. However, this is not the case: equipment is now available which renders the X-ray spectrochemical analysis about as easy in routine application as the optical one. This situation is a consequence of the fact that X-ray techniques as applied to another method of chemical and physical analysis, viz. X-ray diffraction, have attained a high degree of perfection and automation during the past decade and have thereby gained a firm footing in many laboratories. It will be pointed out below that the measurement of radiation intensities by counter tubes in these techniques, instead of the earlier prevailing recording by photographic methods, has played an essential part in the development of X-ray spectrochemical analysis.

Foundations of the method

The origin of the characteristic X-ray spectra may be briefly summarized as follows²⁾. According to the Bohr model, the electron orbits of each atom are arranged in shells, viz. the K, L, M, . . . shells. When the atom is given sufficient energy, an electron may be ejected from one of the inner shells. The place of this electron will then promptly be filled by an electron from an outer shell, whose place will in turn be taken by an electron still farther out, etc. The atom thus returns to its normal state in a series of steps, in each of which a photon is emitted. The energy differences between the electron orbits in different shells are such that these photons have wavelengths in the X-ray region, ranging from a few tenths of an angstrom to some dozens of angstroms.

The characteristic emission spectra arising in this way from different elements consist of comparatively few lines owing to the small number of electron orbits participating. Moreover they are very much alike in general structure, revealing a simple variation in wavelengths which is governed by the atomic number of the element. These facts were first established by the experiments of the English physicist Moseley in 1913/14. Fig. 2 shows a series of X-ray spectra as recorded by Moseley. The very regular trend of the wavelength for each spectral line as a function of the atomic number is shown by fig. 3. These curves are the basis of X-ray spectrochemical qualitative analysis. A comparison of the *intensities* of the spectral lines of the elements

in a mixture or compound will permit a *quantitative* analysis of their concentrations.

In the practical application of X-ray spectrochemical analysis there are two major problems

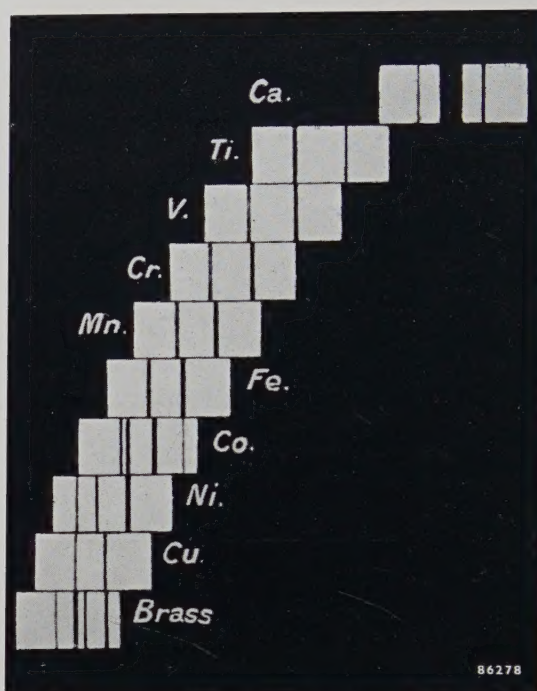


Fig. 2. X-ray spectra of a number of elements photographed by Moseley. (From Phil. Mag. 26, 1024, 1913.)

which should be briefly considered here before going into the details of the present-day technique, viz. the *excitation* of the X-ray spectra and their *analysis*.

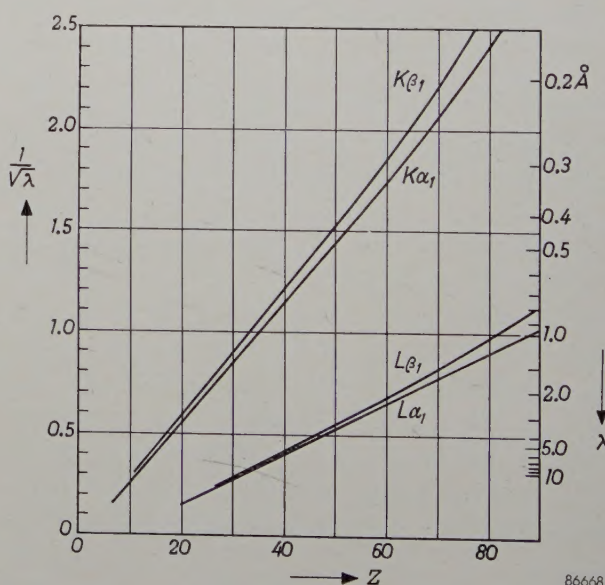


Fig. 3. Wavelengths λ of characteristic X-ray spectral lines of elements, plotted against atomic number Z . According to Moseley's law, there should be a linear relationship between $1/\sqrt{\lambda}$ and Z .

²⁾ For a more complete account and a general treatment of the physics of X-ray spectra see for example: M. Siegbahn, *Spektroskopie der Röntgenstrahlen*, Springer, Berlin 1931. A. H. Compton and S. K. Allison, *X-rays in theory and experiment*, Van Nostrand, New York 1935.

An atom can receive the energy required for the ejection of an electron from an inner shell either by collision with a high-energy free electron or by absorption of a high-energy photon (X-ray quantum). Accordingly there are two ways of exciting the characteristic X-ray spectrum of each element, viz. either by bombarding the specimen with electrons accelerated by a high voltage or by irradiating it with a beam of X-rays. The latter process, called *fluorescence* because of the analogy with the optical case, is now used and in fact has given its name to the whole method of X-ray spectrochemical analysis, which is usually referred to as "X-ray fluorescence analysis".

The first mentioned process of exciting characteristic spectra — by electron bombardment — is that used in X-ray tubes for generating the monochromatic X-rays applied in diffraction analysis (e.g. the K-radiation of copper). In order to utilize this process for spectrochemical analysis each specimen has to be made in the form of a target and introduced as the anode into a type of demountable X-ray tube. The method was applied for a long time in the investigation of characteristic spectra by Siegbahn and others. The element hafnium was discovered by Von Hevesy and Coster in 1923 using this method, and the method was again used when the element was first prepared in a ductile state in the Philips Laboratories at Eindhoven³). It is clear, however, that the difficulties of the technique with demountable X-ray tubes virtually prohibited its large-scale application to routine analysis. Moreover, serious quantitative errors were liable to occur owing to the fact that the specimen exposed to the electron bombardment might volatilize or melt in such a way that the elemental composition at its surface would be altered. For this reason, Von Hevesy and others prior to 1930 had used fluorescence excitation but in order to get sufficient intensity they had to place the specimen very near to the primary X-ray target, inside the tube; the difficulties of vacuum technique etc. thus remained³).

In addition to the characteristic line spectrum, a continuous, nearly structureless X-ray spectrum is generated in a target bombarded by electrons. (This continuous spectrum is due to deceleration of the impinging electrons and is used in medical and other X-ray applications where the polychromatic character of the radiation is not objectionable — or is even desired.) It is important to note that a specimen excited by fluorescence does not emit a continuous

spectrum. On the other hand, the primary X-ray beam used for exciting fluorescence always contains the continuum. This and other details of the fluorescence excitation method actually used will be discussed later.

Spectrochemical analysis by means of spectra excited by electron bombardment is still applied in one special instance, viz. in the testing for spectral purity of X-ray tubes used for diffraction. Impurities in the target contribute X-rays of undesirable wavelengths. Spectroscopic investigation of these radiations yields the necessary information concerning the nature of the impurities. At the same time, fluorescent X-rays emitted by portions of the tube other than the target can be detected. An example of this application of spectrochemical analysis will be seen later in fig. 7b.

The *analysis* of the X-ray spectra is usually effected by applying the principle of diffraction. Mechanically ruled diffraction gratings, which are commonly used for optical spectrographs, can only with great difficulty be made fine enough for the much shorter X-ray wavelengths. A single crystal of a suitable material is used instead. It was Von Laue's discovery of the diffraction of X-rays by crystals which enabled Moseley to carry out his basic experiments on X-ray spectra. The diffraction by a crystal is governed by the well-known Bragg condition:

$$n\lambda = 2d \sin \theta; \quad n = 1, 2, 3, \dots \quad (1)$$

A set of atomic planes of the crystal lattice spaced apart a distance d will "reflect" the X-ray beam of wavelength λ only (if at all) at incident angles θ meeting this condition. (A reflected ray will then make an angle 2θ with the incident ray.) If for the moment the possibility of reflections of different orders (n) is disregarded, reflection for a given wavelength will occur at only one sharply defined angular setting of the crystal. In order to obtain the complete emission spectrum of the specimen, the crystal has to be rotated to scan the desired angular region.

The resulting arrangement for the analysis of the fluorescent X-ray spectrum is schematically shown in fig. 4a. This arrangement is quite similar to that used in X-ray diffractometry, which is similarly based upon the Bragg equation (fig. 4b). In diffractometry, however, a *single known wavelength is used to analyze a diffracting specimen for all d -spacings present*, whereas in spectrochemical analysis a *single known d -spacing of a diffracting crystal is used to analyze the spectrum of the specimen for all wavelengths present*. Thus, in diffractometry the specimen is rotated and the different angles 2θ at which diffracted energy is detected are related to

³) G. von Hevesy, *Chemical analysis by X-rays and its applications*, McGraw Hill, New York, 1932. J. H. de Boer and J. D. Fast, *Z. an. allg. Chem.* **187**, 193-208, 1930.

different d -values. In spectrochemical analysis the crystal is rotated and the different angles 2θ at which diffracted energy is detected are related to different wavelengths.

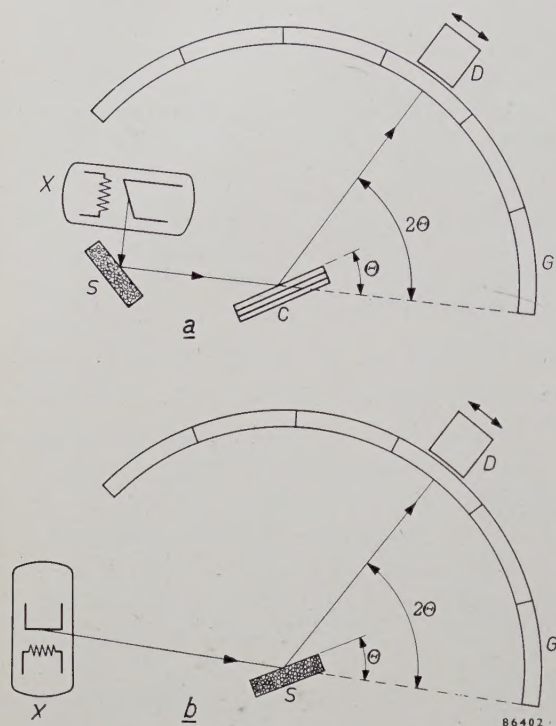


Fig. 4. Schematic arrangement *a*) for X-ray spectrochemical analysis, *b*) for powder diffractometry. X X-ray tube, S specimen, C analyzing crystal, D detector, G goniometer.

Because of the evident similarity in instrumentation between X-ray spectrochemical analysis and X-ray diffractometry, it will be useful to emphasize the difference in the information that can be obtained from these methods. X-ray diffraction patterns reveal differences in the character, dimensions and orientations of crystals. Hence, diffraction analysis identifies compounds by their specific crystal structure and lattice spacings; it distinguishes between different crystalline modifications of elements (e.g. graphite and diamond); it permits quantitative analysis of mixtures of crystallized substances; it distinguishes between mixtures and solid solutions; and it gives information on the orientation of crystallites in a sample, on strain and on crystallite size. Clearly, diffraction methods are mainly applied to matter in the crystalline state.

The characteristic X-ray spectra, on the other hand, are emitted by the atoms of an element regardless of the crystal structure or chemical composition of the sample in which the element occurs and independent of the physical conditions

of the sample. The X-ray spectrographic analysis therefore supplements the diffraction analysis in giving information on the elemental constitution of a sample.

Details of the technique

In embarking on a more detailed description of the equipment and technique, it is convenient to continue the discussion of the actual measurement and recording of the X-ray spectra begun in the preceding section, and to return later to the excitation and other details of the technique. It should be pointed out that in this description it will not be possible to mention all the procedures now in use.

Recording of the spectra

The X-ray energy reflected by the analyzing crystal at different angles can be recorded photographically (which was the original method used by Moseley and others), but the modern technique of using Geiger-Müller tubes or other counter tubes is much better adapted to the purpose. These give an immediate evaluation of the line intensities, which are important for quantitative chemical analysis and which are much more difficult to determine from photographically recorded spectra ⁴⁾ ⁵⁾.

To make this point clearer, we should turn for a moment to the field of X-ray diffraction analysis proper. The method most widely adopted for routine analyses in this field is the Debye-Scherrer method, in which a finely powdered specimen is used: such a specimen, in principle, does not have to be rotated to yield the complete diffraction pattern, since in each angular position of the specimen all possible orientations (Bragg angles θ) with respect to the fixed incident beam are represented among the numerous crystallites. All the diffraction lines belonging to different d -spacings are thus recorded simultaneously on a photographic film laid around the specimen. With a counter tube substituted for the film, on the contrary, scanning of the pattern is evidently necessary, and it must be performed at a relatively low rate, in order to accumulate enough counts at each Bragg angle ⁵⁾. This apparent drawback of "diffractometry" with a counter tube detector has not prevented it from acquiring considerable importance: the reason for this must be attributed to the advantage of easy and accurate intensity evaluation and to the development of a highly

⁴⁾ W. Parrish, E. A. Hamacher and K. Lowitzsch, The "Norelco" X-ray diffractometer, Philips tech. Rev. **16**, 123-133, 1954/1955.

⁵⁾ W. Parrish, X-ray intensity measurements with counter tubes, Philips tech. Rev. **17**, 206-221, 1955/1956 (No. 7-8).

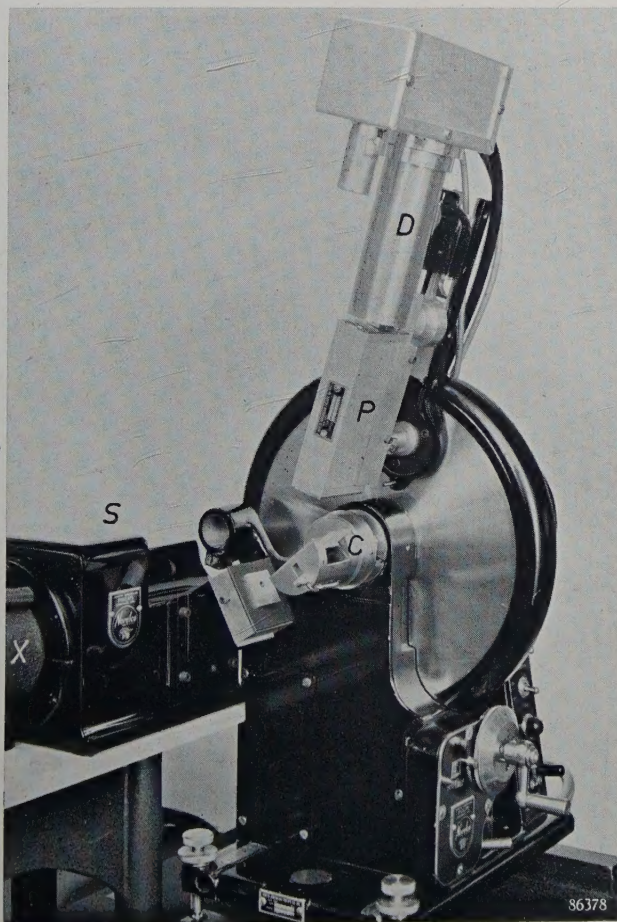


Fig. 5. a) "Norelco" equipment both for X-ray diffraction and X-ray spectrochemical analysis. The X-ray generator, with powder cameras and a goniometer for diffractometry on top of it, is shown in the left; the X-ray spectrograph for spectrochemical analysis is in the middle; the electronic circuits rack including the counting-rate meter and recorder is on the right. The same X-ray generator and electronic circuits are used for both methods but the methods cannot be used simultaneously. b) Goniometer arranged for spectrochemical analysis: *X* horizontally mounted X-ray tube, *S* specimen chamber, *C* analyzing crystal, *P* parallel slit system, *D* radiation detector (scintillation counter).

perfected instrumentation permitting very good angular resolution and accuracy ⁴⁾ ⁵⁾ ⁶⁾.

The determination of intensities from a photographically recorded diffraction pattern being a rather time-consuming process, it is found on balance that diffractometry gives a noticeable saving in time. It is clear that this advantage will be even more pronounced in those cases where only a few lines have to be measured instead of a complete pattern. This is exactly what is usually encountered in spectrochemical analysis: only one characteristic spectral line need be measured for each element, and in many cases the elements whose concentration is to be measured will be known, so that only a very limited angular region need be scanned. The simul-

⁶⁾ E. A. Hamacher and K. Lowitzsch, The "Norelco" counting-rate computer, Philips tech. Rev. 17, 249-254, 1955/56 (No. 9).

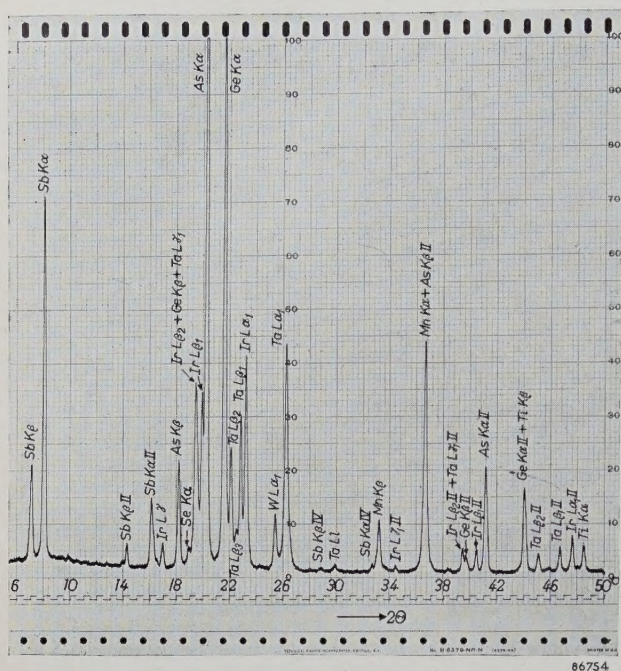


Fig. 6. Qualitative analysis of a mixture of several elements using a quartz analyzing crystal (1011-plane), scintillation counter, scanning speed $\frac{1}{2}^\circ$ per minute. The K-spectra of 22 Ti, 25 Mn, 32 Ge, 33 As, 34 Se, 51 Sb and the L-spectra of 73 Ta, 74 W and 77 Ir can be seen. (The higher order reflections are indicated by Roman numerals.)

taneous rapid development of diffractometry and of X-ray spectrochemical analysis is, therefore, not

to be regarded as being a mere coincidence ⁷⁾.

The close relationship between X-ray spectrochemical analysis and diffractometry is clearly seen in fig. 5, which shows the "Norelco" equipment for X-ray spectrochemical analysis. Except for the fluorescent specimen holder and the X-ray optics, it comprises the same elements as the "Norelco" diffractometer ⁴⁾.

The usual procedure in the analysis of a specimen of unknown composition is first to make a qualitative analysis with the recording counting-rate meter by scanning the entire spectrum at a moderate speed, say $\frac{1}{2}^\circ$ or $\frac{1}{4}^\circ$ (2θ) per minute. This permits identification of the elements present and allows an approximate measure of the concentrations; see fig. 6. Exact measurements are then made by setting the counter tube on the peak of one line selected for each element, and the intensities measured using either fixed-time or fixed-count methods ^{5) 6)}. The background is measured separately and subtracted from the peak intensities.

⁷⁾ The advantage of the counter tube detector when looking for a specific spectral line is so marked that techniques of this nature have been commonly applied also in optical spectrochemical analysis. An early application of this method for monitoring purposes was described in this Review several years ago: O. G. Koppius, An application of Geiger counter tubes for spectrochemical analysis, Philips tech. Rev. 11, 215-222, 1949/50.

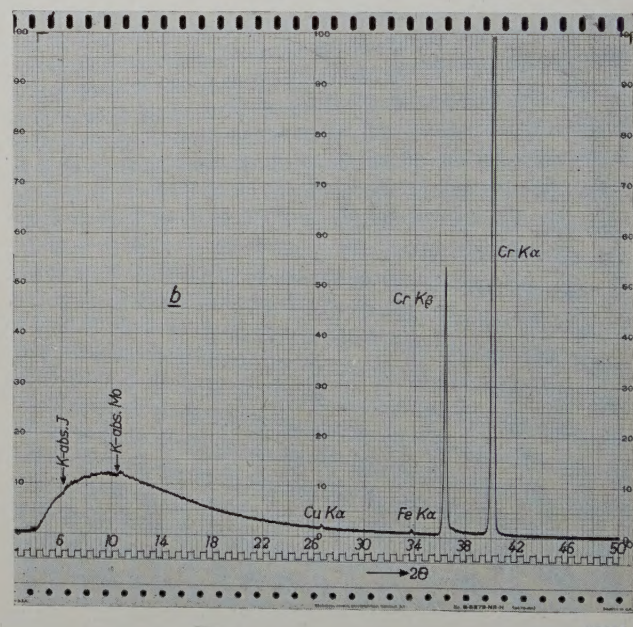
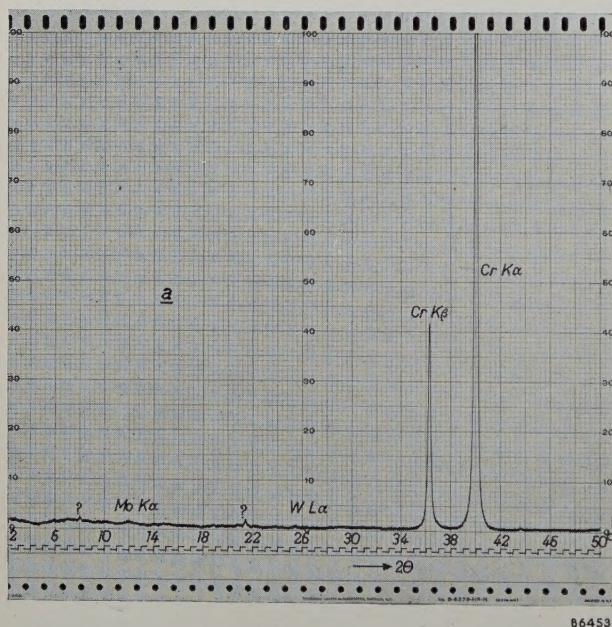


Fig. 7. a) Chromium spectrum produced by X-rays from a tungsten target tube (fluorescence) operated at 50 kV peak. No continuous spectrum is excited in this case.

The weak W Lα line is due to scattering of the primary X-ray beam by the specimen and crystal. (The lines at 8° and 21.5° marked "?" have not been identified).

b) The characteristic K-spectrum of chromium produced by direct electron excitation at 50 kV peak. The spectrum is superimposed upon the continuous spectrum. The X-ray tube current was made smaller than in (a) by a factor such that approximately the same intensity of the Cr K-radiation was obtained.

The two absorption edges are due to iodine (in the scintillation crystal) and molybdenum (in the slits). The copper and iron lines are due to impurities in the target.

Excitation of the spectra

In the present equipment, for an electron beam of given power, the intensity of the X-ray spectral lines when excited by fluorescence will be smaller by a factor of roughly 1000 than when direct excitation by the electron beam is used. The convenient method of fluorescence excitation has therefore become possible in practice only by the development of high power X-ray tubes, very sensitive detectors and suitable X-ray optics. It would, however, be misleading to compare the two methods of excitation merely on the basis of the intensity difference. The intensity is important with a view to the time that will be necessary to measure it: a certain number of quanta (counts) has to be accumulated in order to sufficiently reduce the statistical error of the measurement (see ⁵). The sensitivity of the analysis, i.e. the lowest detectable concentration of admixtures in a specimen, however, will depend on the peak-to-background ratio of the spectral lines. This ratio is generally much higher in the fluorescent spectra than in the directly excited spectra, owing to the absence of the continuous X-ray spectrum. The difference in the spectra is clearly brought out by fig. 7.

The question arises, what kind of primary X-radiation will be most suitable for exciting fluorescence?

It was mentioned above that the primary X-ray target will always emit a continuous spectrum. This spectrum for a given accelerating voltage V of the electrons begins abruptly at a wavelength λ_{\min} , rises to a broad maximum and falls off gradually with increasing wavelength (fig. 8); the

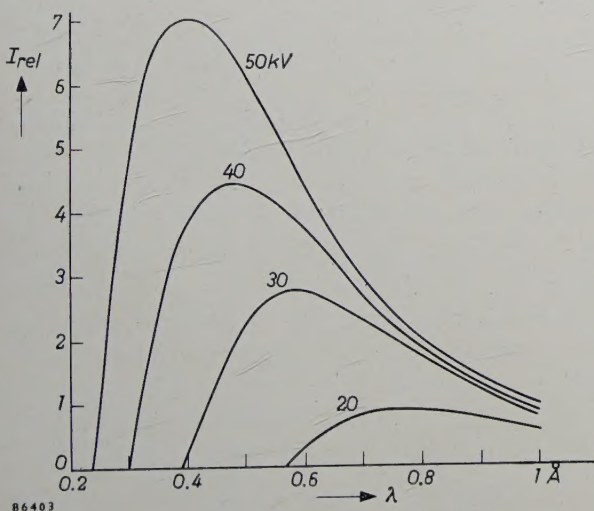


Fig. 8. The continuous spectrum of a tungsten target X-ray tube (relative intensity I_{rel} vs. wavelength λ) obtained with various voltages (peak values) and the same tube current. The curves were redrawn from separate rate meter recordings. Experimental conditions: full-wave rectification, silicon crystal analyzer (111-plane), scintillation counter.

limiting wavelength (in Å) is related to the voltage (in kV) by the equation:

$$V = 12.35/\lambda_{\min} \quad (2)$$

As the voltage is increased (which will increase the amount of energy eV carried by each electron) the limit of the spectrum shifts towards shorter wavelengths. As soon as the energy eV exceeds the energy required to remove an electron from an orbit in, say, the M-shell of a target atom, all the M-lines of the characteristic target spectrum terminating in this orbit will be emitted in addition to the continuum. On further increasing the voltage, the intensities of the M-lines will increase rapidly, and again at a certain voltage groups of lines of the L-series will appear. At a still higher voltage the K-series will appear.

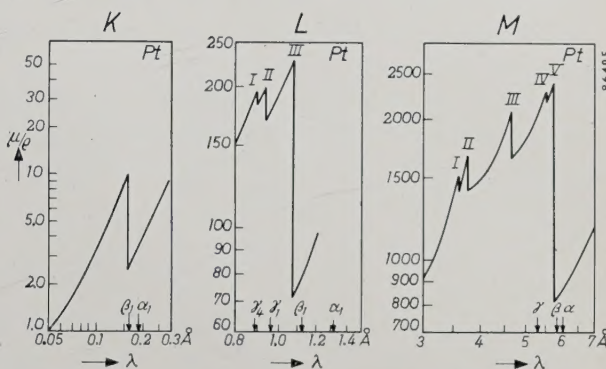


Fig. 9. Mass absorption coefficient (μ/ρ) of platinum as a function of wavelength λ in the regions of the K, L and M absorption edges. Some characteristic emission lines of the K, L and M series of platinum are shown with arrows.

Similar considerations apply to the secondary target, i.e. the specimen, onto which the primary X-ray beam will be directed. Primary radiation in a broad wavelength region will be more or less absorbed by the specimen. With decreasing wavelength, the impinging photons will carry more energy and when a certain wavelength λ_{\min} , characteristic of the element is reached, this energy will be sufficient to knock an electron out of one of the orbits, say of the M-shell. A group of M-lines will then simultaneously be excited and at this wavelength (or rather at a slightly shorter one) the absorption vs. wavelength function of the element shows a steep rise (absorption edge). At still shorter wavelengths, other absorption edges corresponding to other orbits occur: each element has five absorption edges for the M-spectrum, three for the L-spectrum and one for the K-spectrum (fig. 9).

For exciting the fluorescence, the primary radiation must evidently have a wavelength shorter than the absorption edge of the spectral lines

selected for the analysis in hand. Continuous as well as characteristic radiation of the primary target can serve the purpose. It should be noted that in order to get a continuous spectrum of short enough wavelengths, the voltage of the X-ray tube must comply with eq. (2), λ_{\min} now representing the selected absorption edge of the element to be analyzed. Thus, to just excite the K-series in an aluminum specimen, a voltage $V = 1.6$ kV on the X-ray tube will suffice, whilst for a uranium specimen a minimum voltage of 115 kV would be necessary. Since the X-ray equipment generally used in X-ray spectrochemical analysis does not provide for tube voltages exceeding about 50 kV, elements with atomic number higher than about 60 (neodymium) can not be analyzed by a K-line. The voltage necessary to excite the L-series, however, is lower, reaching only 21.7 kV for uranium, so that L-lines can be used for the elements of higher atomic number.

A closer consideration of limitations of the method due to the voltage and other factors will be given below. A number of typical wavelength data are compiled in Table I⁸⁾.

Table I. Characteristic X-ray wavelengths (in Å) of some elements.

Element	K-abs. edge	$K\beta_1$	$K\alpha_1$	LIII abs. edge	$L\gamma_1$	$L\beta_1$	$L\alpha_1$
13 Al	7.951	7.981	8.338				
24 Cr	2.070	2.085	2.290	20.7		21.32	21.71
29 Cu	1.381	1.392	1.540	13.29		13.08	13.36
40 Zr	0.688	0.701	0.786	5.58	5.38	5.84	6.07
60 Nd	0.285	0.294	0.332	1.995	1.878	2.166	2.370
74 W	0.178	0.184	0.209	1.215	1.098	1.282	1.476
92 U	0.107	0.111	0.126	0.722	0.615	0.720	0.911

The continuous spectrum emitted by the primary target may have several times more total energy than its characteristic spectrum (cf. fig. 7b). The ratio depends mainly on the voltage; for a copper target at 50 kV, the energy of the continuum is about an order of magnitude greater than that of the $K\alpha$ lines. Since, however, the fluorescence of the specimen is mainly excited by the radiation closest to its absorption edge, the characteristic lines in the primary radiation can play an important role. The L-spectrum of tungsten, (which is seen in

fig. 1b) for example, is very important in exciting K-fluorescence of the elements from about 34 Se to 25 Mn. In one specific case, viz., nickel excited by a tungsten target tube at 40 kV (with full wave rectification), only about 10% of the Ni $K\alpha$ intensity was found to be due to the continuum of the tungsten target: 40% was due to the La_1 , a_2 lines and 50% to the $L\beta$ and $L\gamma$ lines of the tungsten. Of course, it will not generally be possible to pick a primary target with lines close to the absorption edges of the elements to be analyzed; in such cases one has to be satisfied with using the continuum for the excitation. Tungsten as a primary target can thus be used for a large group of elements, and fluorescence intensities of up to 4×10^6 counts per second may then be obtained from large pure specimens. Tungsten radiation should, however, not be used for the analysis of tungsten in a specimen, and in general any specimen element should not be excited by the identical element as the primary target. The reason for this is that the primary radiation — the continuum as well as the line spectrum — is scattered by the specimen and the analyzing crystal to some extent and will therefore appear in the spectrogram with a certain intensity (cf. fig. 7a), usually less than 1% of the principal fluorescent lines of the specimen. Clearly, the contribution due to a scattered primary W L-line would not be distinguishable from the fluorescent intensity of the same W L-line.

It should be mentioned that owing to the regular dependence of the absorption edges on the atomic number, a method of chemical analysis can also be based on locating these edges for a specimen. Measurement of the absorption coefficient with monochromatic or in some cases polychromatic X-ray beams allows of quantitative analysis. This method, which is much more restricted in its performance than the analysis based on the emission spectra, will not be discussed here⁹⁾.

The X-ray tube

The X-ray tube providing the primary beam is similar to that used in X-ray diffraction work, with the main exception that the focus is of much larger size, viz. about 10×5 mm, and that it is not viewed at a very small angle (the viewing angle is 20°). Indeed, contrary to applications where the X-ray source is used for obtaining *images* (either shadowgraphs as in diagnostics or "slit-images" as in diffraction), there is no point in using a point-source for the irradiation of the fluorescent specimen. A larger focal spot has the advantage of permitting higher loadings. The permissible loading, of course,

⁸⁾ A complete list of X-ray wavelengths has been published by Y. Cauchois and H. Hulubei, *Longueurs d'onde des émissions X et des discontinuités d'absorption X*, Hermann & Cie, Paris 1947. The excitation potentials are given by S. Fine and C. F. Hendee, *Nucleonics* **13**, 36-37, 1955 (No. 3).

⁹⁾ A. Engström, *Acta Radiologica*, Supp. **63**, 1946. H. A. Liebhafsky, *Anal. Chem.* **21**, 17-34, 1949; **22**, 15-16, 1950. **23**, 14-16, 1951; **24**, 16-20, 1952; **25**, 689-692, 1953. B. Lindström, *Acta Radiologica*, Supp. **125**, 1955.

also depends on the thermal conductivity and melting point of the selected primary target metal. For tungsten in the water-cooled "Norelco" tube, a 10×5 mm focal spot permits continuous loading up to 3.5 kW as compared to 1 kW with a 10×1.6 mm focal spot used for diffraction.

The choice of the voltage for operating the X-ray tube is an important point. When the selection of a primary target with a suitable line spectrum for the fluorescence excitation is not possible and the continuous spectrum of a tungsten target has to be used, it will usually be desirable to run the tube at the highest permissible voltage. This will ensure that the largest possible number of unknown elements in the specimen will be excited to fluoresce. It will also ensure the greatest possible intensity of fluorescence of each element, since with increasing tube voltage the portion of the continuum having wavelengths shorter than a given absorption edge will increase (cf. fig. 8).

In two cases the X-ray tube voltage should be made lower than the available maximum, viz. *a*) when it is desirable not to excite fluorescence of *all* elements in the specimen (selective excitation; this case will be considered more closely in the Appendix); *b*) when very long wavelength fluorescence spectra are to be excited. The reason in this latter case is the scattering of the primary radiation through the system. The peak-to-background ratio will be smaller at higher voltages since, for equal X-ray tube power, the height of the maximum (and hence the integrated intensity) of the continuum will increase more than the intensity in a longer wavelength region (fig. 8).

It should be pointed out that for selective excitation and in general when using relatively low tube voltages, it will be advantageous to operate the X-ray tube at constant potential instead of with the more usual full-wave rectified supply. With the latter mode of operation, the continuous X-ray spectrum produced will shift back and forth during each half cycle and will attain its extreme short wavelength position only during the peak of the operating voltage. A specimen element having its excitation potential not far below the peak voltage of the tube will therefore be excited only during a short part of the cycle. The gain in intensity obtained for the $K\alpha$ line of a number of target elements when operating the X-ray tube at a constant potential of 30 kV rather than at a full-wave rectified voltage of 30 kV peak, is plotted in fig. 10.

In comparing the modes of operation it is of course necessary to take into account the power rating of the apparatus available. The "Norelco" diffraction unit is full-wave rectified with a rating of 2.5 kW, while the PW1010 unit made by Philips in Europe gives constant potential with a rating of 1 kW. Similar considerations determine the feasibility of lowering the X-ray tube voltage, since this will necessitate higher tube currents to maintain the power at the same level. With the sealed-off X-ray tubes available for this application and the

"Norelco" power unit, the maximum tube currents are about 50 mA; full use of the power available from the "Norelco" unit therefore cannot be achieved at voltages below 50 kV.

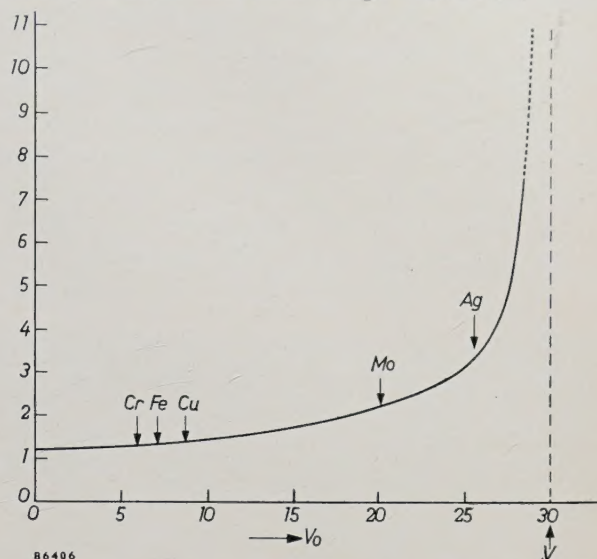


Fig. 10. The gain in line intensity of the primary beam obtained by operating the X-ray tube at constant potential V instead of with full-wave rectified voltage of peak value V , is plotted against the critical excitation potential V_0 . The curve shown was calculated on the basis of $V = 30$ kV, assuming the intensity increases with $(V - V_0)^2$ and neglecting self-absorption in the target. The gain factor increases with critical excitation potential V_0 of the elements; a few typical elements are indicated. The gain factor also increases as the operating voltage V is decreased.

At low voltages it is particularly important to have an X-ray tube window transmitting the primary X-ray beam without much loss. The beryllium windows normally used vary in thickness from about 1.5 to 1 mm and will transmit X-rays up to 3 or 4 Å as can be seen in fig. 11.

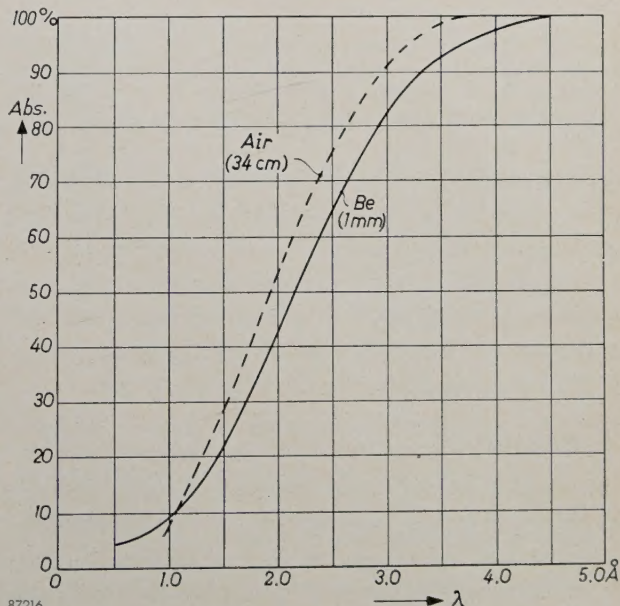


Fig. 11. The percentage absorption of a 1 mm thick beryllium window and of an air path 34 cm long (i.e. about the length used in the "Norelco" spectrograph) as a function of wavelength λ of the X-rays.

These soft X-rays are appreciably absorbed in air so that large intensity losses would occur. The air absorption in a 34 cm path (as used in the "Norelco" equipment) is also shown in fig. 11. The air absorption problem in the goniometer for fluorescent radiation of these and even longer wavelengths can be solved in a simple way by introducing helium in the place of air into the X-ray optical path. This is done by attaching a flexible rubber bag or polyethylene sleeve to the goniometer and passing helium through the system, see fig. 12; a trans-

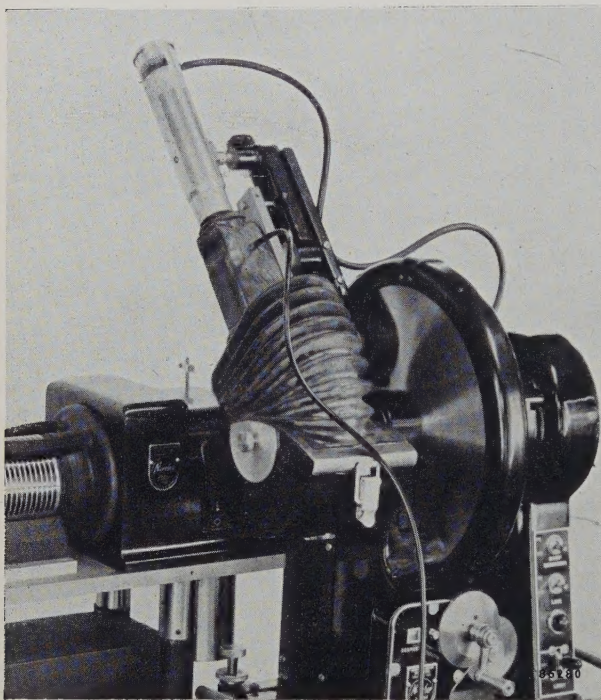


Fig. 12. "Norelco" helium attachment. By passing helium through the rubber-enclosed X-ray path, the serious loss of intensity due to absorption of soft X-rays in air is reduced. This avoids the necessity of using vacuum techniques.

mission of about 85% for aluminium $K\alpha$ radiation of $\lambda = 8.3 \text{ \AA}$ is thus obtained in the "Norelco" goniometer. Where helium is not readily available, a vacuum path can be used. In this case two more windows are practically unavoidable; thin "Mylar" polyester film has been used for the purpose, a sheet of 0.06 mm absorbing about 45% of Al $K\alpha$.

X-ray optics

In order to collect sufficient radiation for the analysis of minor constituents, it is desirable to have a large specimen surface acting as a source. It is *not* possible (without reducing the radiation collected) to render the *apparent* fluorescent source small by viewing the specimen at a very small angle to the surface.

The well-known expedient of decreasing the apparent size, which is employed in nearly every application of X-rays in order to obtain a high brilliance point or line source (cf. above), is only applicable to electron-excited targets. The electrons are stopped at a relatively small depth, usually a fraction of a micron under the surface, so that only a thin layer of the target acts as an X-ray source. This layer is practically transparent to the emitted X-rays, even to those travelling obliquely. In the case of fluorescence, on the other hand, the primary X-rays which excite the fluorescent X-rays penetrate to a considerable depth in the specimen before being absorbed and the latter will equally absorb the emitted rays. Consequently no gain in brilliance is obtained by using small glancing angles (the specimen is a Lambert type source).

A fluorescent source of large apparent size precludes the possibility of using a focussing arrangement like that used in diffractometry⁴⁾. The arrangement applied in most cases and also in the "Norelco" equipment is shown in fig. 13¹⁰⁾. The analyzer is a large flat single-crystal plate, of width about 1 in. and length L about 3 in. In a position of the crystal corresponding to the Bragg angle θ for a particular fluorescent line (cf. eq. 1) each part of the large specimen will have its radiation reflected by a particular zone of the crystal, as indicated in the figure. The receiving window of the detector must be wide enough to take in all the (nearly) parallel reflected rays. The whole system can be visualized as consisting of a great number of systems acting in parallel narrow beams, separated by the set of parallel thin metal foils (parallel slit

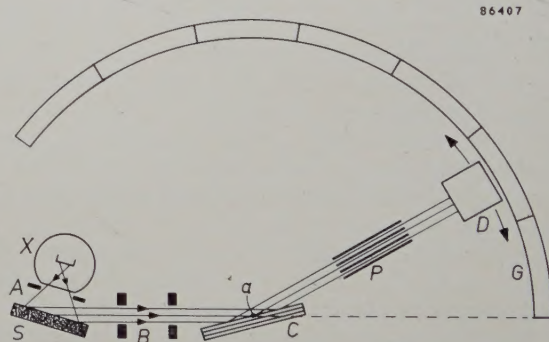


Fig. 13. Non-focussing X-ray optics used for fluorescence analysis of large specimens. S specimen excited by primary radiation from X-ray tube X; C analyzing crystal which is rotated around axis a in order to scan different wavelengths. The detector D is rotated on the goniometer G at twice the angular speed of the crystal. The parallel slit system P ensures the required angular resolution; the latter is approximately determined by the angular aperture 2α of the slits ($\tan \alpha = s/l$, where l is the length and s the spacing of the foils). The slits A and B reduce scattered radiation. (It should be noted that the parallel slit system has a function here different from its function in the diffractometer optics; its orientation is perpendicular to that in the diffractometer⁴⁾. Friedman and Birks¹⁰⁾ employed tubes in place of flat foils.)

¹⁰⁾ An arrangement employing similar principles was first described by H. Friedman and L. S. Birks, A Geiger counter spectrometer for X-ray fluorescence analysis, *Rev. sci. Instr.* **19**, 323-330, 1948.

system) which are positioned between crystal and detector. The role of these metal partitions can be explained as follows (*fig. 14*). Imagine the incident and reflected rays for one value of angle θ as material lines rigidly fixed to each part of the analyzing

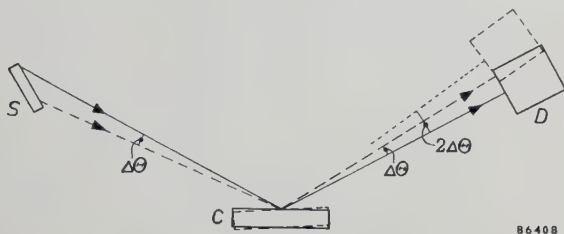


Fig. 14. When the parallel slit system is omitted, the analyzing crystal when being rotated will continue to contribute rays reflected at a given angle θ , within a certain angular region $\Delta\theta$ determined by the size of the specimen. The region is limited by the introduction of the parallel slit system.

crystal. When the latter is rotated, the lines representing the incident rays will "sweep" over the specimen. These rays will continue to "see" the source within a certain angular region $\Delta\theta$ of the crystal. This region would be the approximate width of the recorded fluorescent line if the partitions were not present, since the wide-window detector, although it is rotated through double the angle $\Delta\theta$, would continue to receive part of the reflected rays. The parallel slit system, however, limits the recorded line width to a reasonable value and therefore provides an acceptable angular resolution, dependent on the angular aperture $2a$ of the slits. For a slit system with $2a = 0.58^\circ$ a line width of $0.69^\circ (2\theta)$ was obtained in a typical case. Reducing $2a$ by a factor of 4 (to 0.15°) improves the resolution by a factor of 3 (line width 0.23°), which is sufficient for most analytical purposes. It also improves the peak-to-background ratio by a factor of 3, but it decreases the intensity by a factor of 2.

If only very small specimens are available, the fluorescent intensity will be much smaller because a much smaller part of the primary radiation is intercepted; it is then necessary to use a larger segment of radiation from the specimen in order to obtain enough counts in a reasonable time. A focussing arrangement as shown in *fig. 15* can then be used. The analyzing crystal has a curved reflecting surface. The specimen (which is a "point" or "line" source in this case), the reflecting surface of the crystal and the receiving slit of the detector all lie on a fixed circle of radius r . To obtain the best focussing¹¹⁾ the crystal is first

bent so that the reflecting atomic planes conform to a circle of radius $2r$, and then the reflecting surface of the bent crystal is ground to the radius r . Scanning of the spectrum is effected by moving both the crystal and the detector around the focussing circle, the former at half the speed of the latter. The detector with its scatter slit is swivelled around the center of the receiving slit by means of a wire-and-pulley device during the movement, so that the detector keeps seeing the whole crystal. This type of X-ray optics has been used for fluorescence analysis of samples in milligram quantities¹²⁾.

The focussing arrangement just described can also be used with large specimens. The tiny specimen of *fig. 15* is then replaced by a fine slit which transmits a segment of radiation from the large specimen placed behind it. This, however, does not give a higher intensity or better resolution than the nonfocussing arrangement of *fig. 13* using a flat crystal.

The detector

The detectors in current use for X-ray spectrochemical analysis are basically the same as used in diffractometry and will be described in a separate article in this Review, so that a few notes will be sufficient here.

The Geiger counter tube has been the detector most commonly used in X-ray diffraction and spectrochemical analysis⁴⁾. In its modern form, using halogen as a quenching gas, it has a sensitive volume sufficiently wide to detect nearly the entire large beam used in the X-ray optics of *fig. 13*. Its principal limitation lies in its long dead time (about 270 microseconds) giving rise to counting losses at

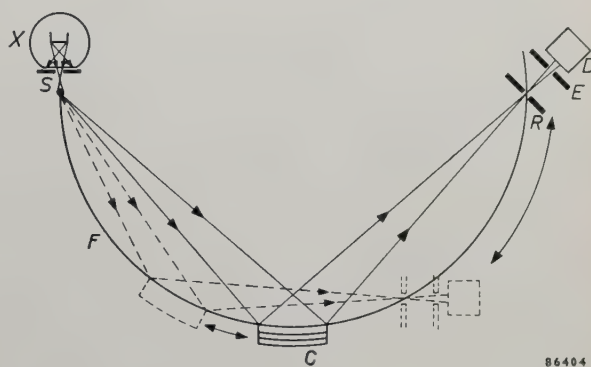


Fig. 15. Focussing X-ray optics used for very small specimens. A curved analyzing crystal C is employed. The specimen S forms a line source (perpendicular to the plane of the drawing). S , C and the receiving slit R of the detector, are situated on the focussing circle F . To measure different wavelengths, the crystal C is moved along F at one half the angular speed of R as shown by the dotted lines, and the detector, with its receiving slit R and anti-scatter slit E is swivelled to point at C ¹²⁾.

¹¹⁾ See, for example, Yvette Cauchois, Recent developments in bent-crystal technique, Trans. Instr. Meas. Conf. Stockholm 1949, 41-45.

¹²⁾ L. S. Birks and E. J. Brooks, Applications of curved-crystal X-ray spectrometers, Anal. Chem. 27, 437-440, 1955 (No. 3).

high intensities, and in its low sensitivity (due to low absorption) for the shorter wavelengths. The proportional counter as developed for X-ray measurements in recent years has about the same spectral sensitivity characteristics as the Geiger counter but a very short dead time ($< 1 \mu\text{sec}$). The most generally useful detector for fluorescence analysis is the scintillation counter. It has the same advantage as the proportional counter in eliminating the dead time problem, and moreover when using an NaI scintillating crystal it has a nearly uniform and high spectral sensitivity throughout the important wavelength region (fig. 16).

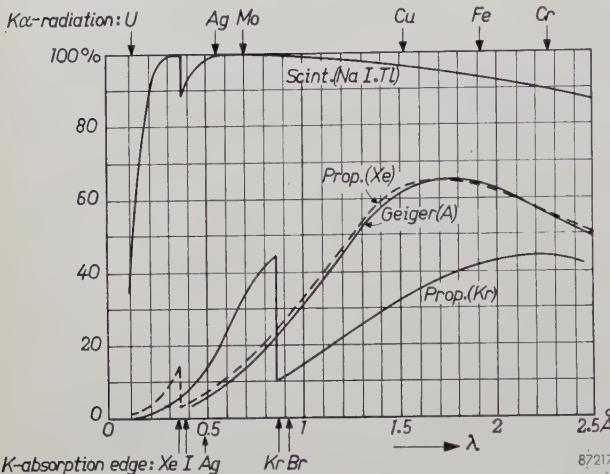


Fig. 16. Calculated quantum counting efficiency (%) as a function of wavelength for several X-ray detectors. Scintillation counter with NaI-Tl crystal 1 mm thick; Geiger counter, "Norelco" 62019, and mica window 13 μ , argon filling at 55 cm Hg, 10 cm in length; proportional counter, side window, beryllium 130 μ + mica 13 μ , xenon at 30 cm Hg, 2.7 cm length; proportional counter, side window, beryllium 130 μ + mica 13 μ , krypton at 50 cm Hg, 2.7 cm length. (From J. Taylor and W. Parrish, Rev. sci. Inst. 26, 367, 1955.)

For the proportional and the scintillation counter, the pulse height produced by an X-ray quantum is proportional to the quantum energy, i.e. inversely proportional to its wavelength. With suitable circuits for pulse height discrimination, this property can be used to great advantage for increasing the peak-to-background ratio and for separating lines in the case of overlapping spectral lines of different elements (see Appendix).

The analyzing crystal

The diffracting crystal used for analyzing the fluorescent spectra has to meet the following requirements.

It must have a chemical composition such that its own fluorescence caused by the impinging fluorescent radiation will not disturb the measurements. When analyzing at wavelengths less than

3 Å, the analyzing crystal should therefore not contain elements with atomic number above 20; the K-radiation of the crystal elements in the analyzer will then have large wavelengths and will be completely absorbed in the air before reaching the detector. When analyzing at longer wavelengths, higher atomic number elements may be used in the analyzing crystal provided that their L-spectra do not occur in the region which is being analyzed (their K-spectra are not excited in this case). The analyzing crystal must be large enough to allow the use of wide beams as shown in fig. 13. Moreover, the reflecting surface must be quite perfect, i.e. free of distortions caused by grinding or cleaving, and the crystal should not have a pronounced mosaic structure, in which several portions have somewhat different angular orientations. Such a structure would spread the angular width of a line corresponding to the spread of orientation of the mosaic portions, it would also reduce the peak intensity and it might even cause the reflections to split up into multiple peaks, thus seriously complicating the interpretation of the spectrum ¹³).

Besides these basic requirements, the analyzing crystal should have a suitable lattice spacing d for the diffraction. For a given wavelength λ , the reflection angle 2θ will be larger the smaller d , according to eq. (1). The d -value should be small enough to make the angle 2θ greater than approximately 10° or 15° even at the shortest wavelength used; otherwise excessively long analyzing crystals would be needed in order to prevent the direct fluorescent beam from entering the detector (see fig. 13). A small d -value is also favorable for producing a large dispersion $d\theta/d\lambda$ of the spectrum, to give good separation of adjacent lines; this is seen by differentiating eq. (1):

$$\frac{d\theta}{d\lambda} = \frac{n}{2d \cos \theta} \cdot \cdot \cdot \cdot \cdot \quad (3)$$

On the other hand, a small d -value will set an upper limit to the range of wavelengths to be analyzed, since at $\lambda = 2d$, the angle 2θ will become 180° . The λ -limit is in fact even lower than $2d$, because the reflection angle range of the goniometer is not 180° but is mechanically limited to about 150° . It will therefore be necessary to select a larger d -value for longer wavelengths.

¹³) The analyzing crystal should not — and in practice never will — be perfect on an atomic scale: slight imperfections in the arrangement of the atoms are required in order to avoid extinction effects which diminish the intensity of the reflection; see for example R. W. James, The optical principles of the diffraction of X-rays, G. Bell and Sons, London 1948.

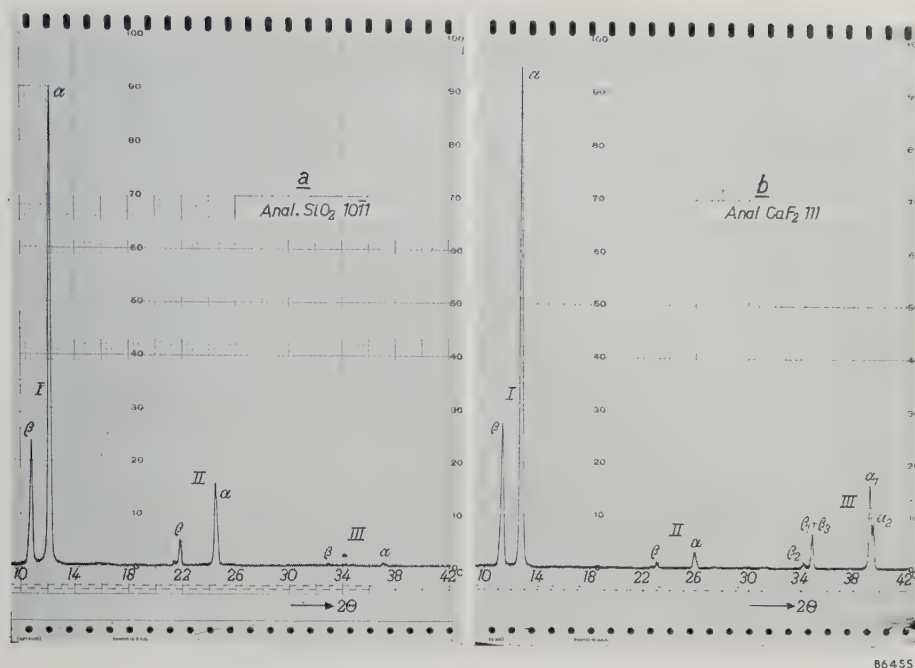


Fig. 17. Molybdenum K-spectrum excited by a tungsten target X-ray tube and reflected by different analyzing crystals. (Nickel filter placed on window of X-ray tube to eliminate scattered L-spectrum of tungsten.) a) Reflection from quartz cut parallel to 1011. b) Reflection from fluorite, cleavage plane 111. The first, second and third orders are indicated by Roman numerals.

A final important requirement refers to the higher order reflections caused by the analyzing crystal. The second order reflection of a radiation with wavelength of $\lambda/2$ and the third order of $\lambda/3$ will occur at the same angle 2θ as the first order reflection of λ . This may result in overlapping of lines originating from different elements and also in a lower peak-to-background ratio when a strong continuum is scattered by the fluorescent specimen. It is desirable in these cases to select a crystal which has very weak or zero second order reflection. An example of this would be silicon or fluorite (CaF_2), both cut parallel to the 111 plane. Both crystals have a third order reflection which is approximately 1/10 as strong as the first order. Fig. 17 shows the difference in the spectra obtained with crystals having different relative intensities of higher order reflections. Table II gives a list of crystals commonly used for X-ray spectrochemical analysis.

Specimens

In the discussion of the X-ray optics it was stated that a large fluorescent specimen surface is desirable for obtaining high intensity reflections with the flat analyzing crystal arrangement. This arrangement can be used, however, also for smaller size samples, down to a few mm diameter. In this case the primary X-ray beam should be stopped down to the actual specimen size in order to avoid an excess of scattered radiation arising in the vicinity

of the specimen holder. If only very small amounts of samples are available, say a few milligrams, it may be necessary to use the focussing crystal arrangement (fig. 15). The specimen may in that case be coated on a thin glass fibre mounted on the focussing circle (or rather, the "focussing cylinder").

The specimen preparation methods for large samples depend on the nature of the specimen, which may vary widely: liquids, powders, solids such as minerals or metals, or thin films can be analyzed. The surface should be flat and clean and the distribution of constituents in it should be

Table II. Some analyzer crystals for X-ray spectrochemical analysis. The first four crystals are most frequently used. For the crystal planes marked * the second order reflection is weak or absent.

Crystal	Reflecting plane used (hkl)	Lattice spacing d in Å	Reflection angle 2θ for $\text{CuK}\alpha$ radiation	Relative intensity
LiF	200	2.01	45.1°	High
SiO_2 (quartz)	10 $\bar{1}$ 1	3.343	26.7	High
NaCl	200	2.820	31.7	High
CaF_2	111*	3.16	28.2	High
Al	111	2.338	38.5	High
"	200	2.026	44.8	Med.
SiO_2 (quartz)	10 $\bar{1}$ 0	4.255	20.9	Med.
"	20 $\bar{2}$ 3	1.375	68.2	Low
"	5052	0.812	143.5	Low
Si	111*	3.135	28.5	High
Mica	002	9.96	8.9	Low

representative of the composition of the whole sample. Adequate polishing and etching are required for metal specimens in order to avoid smearing of one component over another. When making casts of molten metals it is important to avoid contamination by the mould. For liquid specimens it is important to prevent volatilization, e.g., by placing an X-ray transparent lid on the container. Equal particle size is desirable in a mixed powder in order to minimize errors due to differences of absorption of fluorescent X-rays by the particles. Another precaution is to minimize the whole inter-particle absorption effect by preparing the powder specimen in the form of a flat solid wafer in a hydraulic press ¹⁴).

The latter factor, i.e., the attenuation of fluorescent X-rays by absorption within the specimen, is of general importance in the analysis. This effect and the subsidiary one that fluorescent rays emitted by one element may contribute to generating fluorescence of another element, cause the relationship between measured fluorescent intensity and concentration of an element in the specimen to be non-linear. For semi-quantitative analyses it is possible to allow roughly for these effects, and in fact no other analytical method is so useful for approximately analyzing wide variations in composition in so short a time. For accurate quantitative analysis by absolute measurements, however, it would be necessary to calculate precisely the effects mentioned, but this is difficult to do except in the simplest cases ¹⁵). The usual way for accurate quantitative analysis, therefore, as in optical spectrochemical analysis, is to prepare a certain number of reference standards, i.e. specimens of known composition in different concentration regions. The standards are used to prepare working calibration curves of X-ray fluorescent intensity as a function of the concentration of each constituent. Only for combinations of elements with nearly equal absorption are the curves relating X-ray intensity to concentration nearly linear ¹⁰). The greater the differences in the absorption, the closer together in composition should the standards be chosen. "Internal" standards prepared by adding known amounts of an element to the specimen are also used in some analyses ¹⁶).

Performance and limitations of the method

The accuracy of the concentrations thus determined will depend not only on the specimen preparation and the calibration curves, but also on the stability of the X-ray source and on the counting statistics involved in the intensity measurements: for good accuracy a large number of counts must be accumulated (this factor and the "counting strategy" were discussed at some length in ⁵). In the largest specimens used for the flat-crystal method (fig. 13), the major constituents usually produce a large enough line peak intensity to accumulate in one minute (of time) the number of counts required to give an accuracy of 1% or better in the analysis. The lower limit of concentrations that can be determined by the method is set by the peak-to-background ratio; it will be obvious from the preceding sections that this ratio will be very different for different cases. With some preliminary wet chemical or physical extraction methods to enhance the peak-to-background ratio, analyses of minor constituents in the region below 10⁻³% may be made with fair accuracy. Successful analyses of constituents of a few parts per million have been reported, and with the focussing arrangement of fig. 15, microgram quantities have been determined in milligram samples with standard deviations of the order of 10 to 15%.

A comparison with optical spectrochemical analysis is useful for an assessment of the value of X-ray spectrochemical analysis. Such a comparison, of course, will reveal different aspects for each specific analytical problem for which the alternative of both methods is offered. In general, it may be said that the X-ray method cannot compete with the optical one in the analysis for trace elements: the optical method will in some cases go down to concentrations of one part in 10⁷. On the other hand, the optical method is less sensitive to differences in the concentration of a major constituent, which are most easily measured by the X-ray method. Another general aspect is the range of elements for which the methods are useful: The optical method is generally used for about 65 or 70 elements scattered all over the periodic system; it is not readily applicable to electronegative elements such as the halogens, sulphur, etc., which have spectra in the far ultraviolet. The X-ray method is useful for all elements above atomic number about 13 but cannot at the moment be applied to the lower end of the periodic table for reasons discussed more fully below. A general advantage of the X-ray method is its non-destructive nature and its ability to cope with all kinds of specimens. It can be applied

¹⁴) Some of the effects of absorption and particle size of powders are discussed by P. M. de Wolff, Part F in "X-Ray Crystallography", Ed. J. Bouman, North-Holland Publ. Co., Amsterdam 1951.

¹⁵) See, for example, J. Sherman, Amer. Soc. Test. Mat., Spec. tech. publ. No. 157, Philadelphia 1954.

¹⁶) J. Adler and J. M. Axelrod, Spectrochim. Acta 7, 91-99, 1955 (No. 2).

to crystalline as well as to amorphous materials, and the specimen can be in the liquid or solid state, in powder or glass or metal form, with constituents dispersed or dissolved. This compares favorably with the optical method on which the specimen imposes certain limitations. From a methodological point of view, finally, it is interesting to compare the ways of handling overlapping spectra. The only way of handling this problem in the optical case is the use of high dispersion, and owing to the complicated character of most optical spectra, this might necessitate the use of grating spectrographs of very great length. In the X-ray case, the spectra, being much simpler, cause much less overlapping, and moreover there are several methods other than increased dispersion for separating adjacent lines. These methods, which in themselves form an interesting survey of the physical phenomena involved in X-ray spectroscopy, are described in the Appendix to this article.

The main *limitations* of X-ray spectrochemical analysis lie in the excitation and handling of radiation of very long or very short wavelengths. Summarizing and amplifying what has been said about these limits in the above, it can be stated that the X-ray fluorescence method is useful for all elements in the periodic system from about 13 Al to 92 U. Instrumentation is simplest and work easiest for the wavelength region between about 2.2 and 0.3 Å, comprising the K-spectra from 25 Mn to 60 Nd and the L-spectra from 62 Sm to 92 U (see *Table III*).

The K-spectra for elements 61 to 92, although even simpler than the L-spectra and therefore desirable, cannot at the moment be used, since for their excitation high primary target voltages (45 kV to 116 kV) would be necessary, for which the available X-ray generators are not suitable. Moreover, the radiation protection problems would be much more serious than at voltages below 50 kV. Finally, even with the smallest *d*-values for the analyzing crystal that can be selected, the reflection angles would be very small (see *Table III*).

For the elements 13 Al to 24 Cr, the K-spectra lying between about 9.0 and 2.3 Å have to be utilized. Radiation of this wavelength region (which also contains some L-spectra and M-spectra of higher atomic number elements) is strongly absorbed in air and will therefore necessitate the helium or vacuum path technique described above.

The K-spectra of elements of atomic number below 13 lie in the ultra-soft X-ray region, which is hardly accessible at the moment. Unfortunately, this group comprises the elements carbon, nitrogen, and oxygen, which are so important for organic and biological studies.

Applications of X-ray spectrochemical analysis

It is impossible to list here the many successful applications of the method to analytical chemical problems in industry. The method has been applied to a wide variety of metallurgical problems, e.g., for the analysis of steels and many types of alloys; in mineralogy for the analysis of ores, minerals and concentrates; and in the petroleum industry for the analysis of sulphur in oil and of bromine in liquid hydrocarbons. A few typical examples are mentioned below.

Birks and others, in 1950, applied the X-ray fluorescence method to the quantitative determination of tetraethyl lead and ethylene bromide in aviation gasoline¹⁷). A one-minute count on the Pb *La* line in a sample containing about 4 ml tetraethyl lead per gal. gave the tetraethyl lead content with a probable error of ± 0.06 ml per gal. Similarly, a one-minute count on the Br *Ka* line gave the ethylene bromide content with a probable error of ± 0.16 ml per gal. in a 1.8 ml per gal. concentration. It was thus possible to make 10 to 20 determinations per hour for both Pb and Br with no special specimen preparation of the liquid and

¹⁷) Anal. Chem. **22**, 1258-1261, 1950.

Table III. Major analytical regions determined by wavelengths and instrumentation.

Wavelength region (Å)	Lowest exciting voltages (KV)	Elements	Spectra (<i>a</i> -lines)	Path	Lattice spacing of analyzer	Detector
9-2.3	1.4-6.5	13 Al - 24 Cr 34 Se - 61 Pm 69 Tu - 92 U	K L M	Helium, or vacuum with thin windows	$d = 4.3$ Å reflects Al <i>Ka</i> at 150°	Prop. counter with thin window; scint. counter below 4 Å
2.2-0.3	6.5-44	25 Mn - 60 Nd 62 Sm - 92 U	K L	Air	$d = 1.5$ Å reflects Ba <i>Ka</i> at 15°	Scint. counter; prop. and Geiger counter above 1 Å.
0.3-0.1	45-116	61 Pm - 92 U	K	Air	$d = 1.5$ Å reflects U <i>Ka</i> at 4.9°	Scintillation counter

achieve the same accuracy as conventional chemical methods¹⁸⁾. X-ray tubes, detectors and techniques recently developed would give even higher accuracy in less time. The method is now widely used for automatic plant control because it is so rapid, accurate and simple.

Small amounts of Ni, Fe and V have a deleterious effect in cracking catalysts. Standard chemical and optical spectrographic methods were found to lack the precision to distinguish between good and poor catalysts. Dyroff and Skiba¹⁹⁾ developed an X-ray fluorescence method for determining these contaminants in silica-alumina catalysts which took about 15 minutes for a complete analysis on samples as small as 2 grams. They achieved a precision of 3% for Fe present in the 0.1 to 1.0 weight % range, and 0.002% (absolute) for Ni and V in the 0.002 to 0.10 weight % range.

Davis and Van Nordstrand²⁰⁾ used the fluorescence method for rapid and accurate control analysis for lubrication oil blending. They obtained an accuracy of 2% to 3% of Ba and Ca in concentrations about 0.05%, and 1% to 2% accuracy of Zn in concentrations greater than 0.005%. It was necessary to prepare several calibration curves for Zn in the various Ba concentrations due to the absorption effects discussed earlier¹⁴⁾. The time for the analysis of each element was 3 to 12 minutes; this is only a fraction of the time required for standard chemical methods, which give no better accuracy.

X-ray fluorescence has proved to be a reliable method for the analysis of Nb and Ta in ore minerals and for following the increase in concentrations during mineral dressing processes²¹⁾. It takes a competent chemist 5 to 15 days to make a chemical analysis for these elements, while 10 to 50 samples can be analyzed with comparable accuracy in a day by the X-ray method.

The method has been applied to small samples, trace element analysis and disperse systems. Thin evaporated films of Ni, Fe and Cr (about 100 Å thick, corresponding to surface densities of 1 to 100×10^{-6} gm/cm² have been analyzed by Rhodin²²⁾ with an accuracy of 2% or better, the results being in excellent agreement with those obtained by microcolorimetric methods.

These are only a few of the applications of the

method. The reader may consult recent volumes of Analytical Chemistry (1950 et seq.) where many specific applications have been published.

To conclude this article, a threefold development of the application of X-ray spectrochemical analysis can be anticipated: a widening of the field within the wavelength regions 0.3 to 2.2 and 2.3 to 9 Å, to include even more analytical problems; a possible extension of the wavelength limit beyond 9 Å, a region where instrumental difficulties become very great, but which is important because it embraces elements involved in organic and bio-chemistry; lastly an intensification in the routine application of the method to specific cases. In fact, the method is capable of a considerable degree of automation, as has been shown by the design of several completely automatic instruments. One of these, the North American Philips "Autrometer", is shown in *fig. 18*.

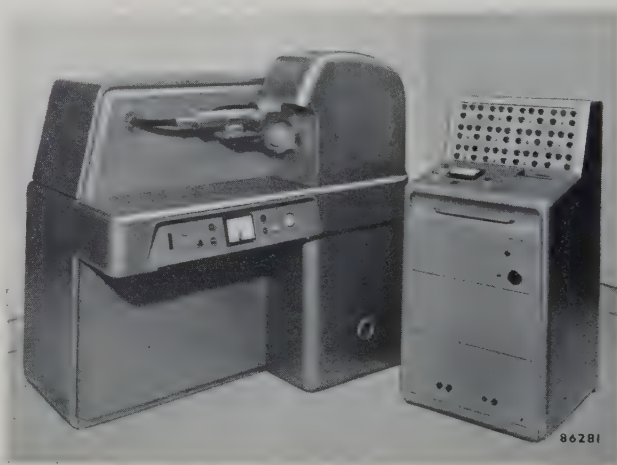


Fig. 18. The "Norelco" "Autrometer", developed for automatic X-ray spectrochemical analysis in industrial plant control. The X-ray unit is on the left and the electronic circuits unit on the right.

In this instrument, the crystal and detector, arranged according to *fig. 13*, are automatically stepped in sequence to a number of preselected Bragg angle positions and the intensities recorded. Once such an instrument has been calibrated, the operation is simple and analyses are performed rapidly so that a very effective solution to industrial production control problems is offered.

Appendix: Methods of handling overlapping lines

Table IV shows some cases of closely spaced X-ray spectral lines. The methods of handling such cases will be illustrated using niobium and tungsten as an example.

The Nb K α line first order reflection and the W L α line, obtained with a flat analyzing quartz crystal (10 $\bar{1}$ 1 plane, $d = 3.34$ Å) and using a parallel slit assembly of angular

¹⁸⁾ In contrast to X-ray *absorption* analysis, other additives and impurities were found to have little effect on the accuracy of the measurements; see *Anal. Chem.* **22**, 1238-1248 and 1248-1258, 1950.

¹⁹⁾ *Anal. Chem.* **26**, 1774-1778, 1954.

²⁰⁾ *Anal. Chem.* **26**, 973-977, 1954.

²¹⁾ *Anal. Chem.* **26**, 800-805, 1954.

²²⁾ *Anal. Chem.* **27**, 1857-1861, 1955.

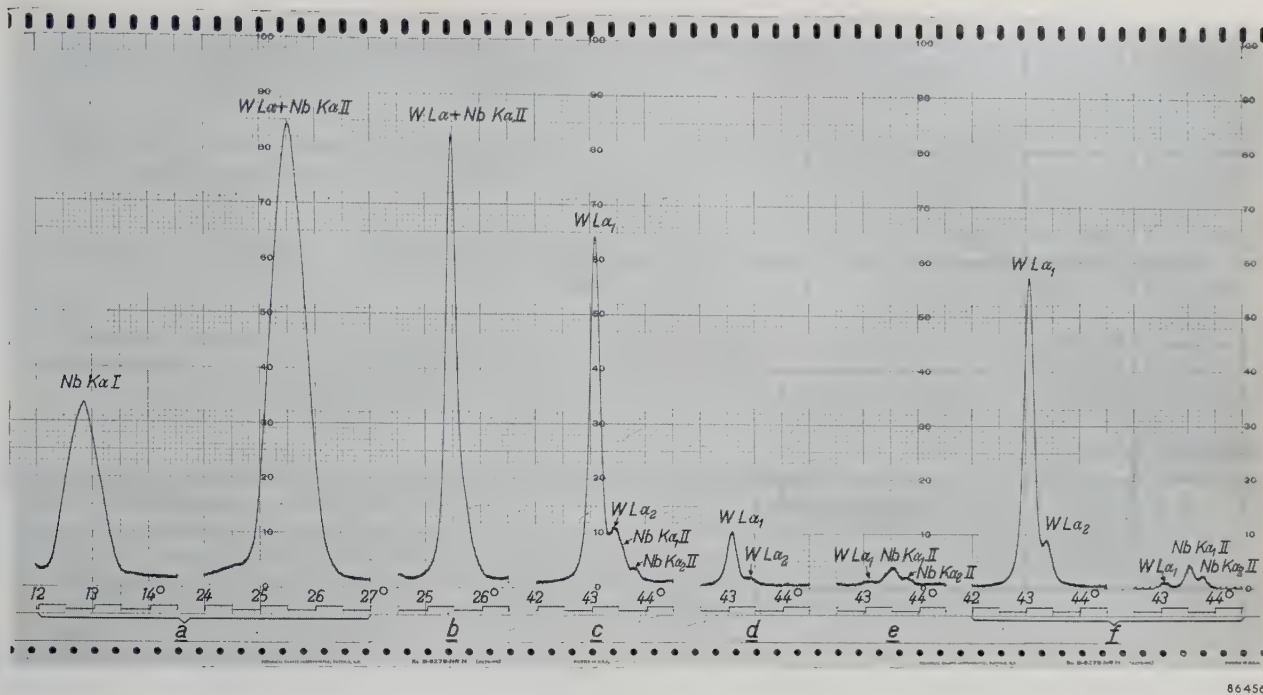


Fig. 19. Methods of separating overlapping spectral lines. The specimen contains WC 72%, TiC 10%, NbC 10%, Co 8%; i.e. approx. W 67.6% and Nb 8.9%. Tungsten target X-ray tube, 50 kV peak, 45 mA (except for method *d*, see below). Full scale intensity = 6400 counts/sec for (a) and 3200 counts/sec for (b-f). Scanning speed $\frac{1}{2}^\circ$ per min, time constant 4 sec, scintillation counter.

(a) Nb Ka and W La + Nb Ka second order reflected from quartz 1011 ($d = 3.34 \text{ \AA}$) with parallel slit system aperture $2a = 0.58^\circ$.

(b) W La + Nb Ka second order as in (a) but $2a = 0.15^\circ$.

(c) W La and Nb Ka second order reflection from lithium fluoride, 200 ($d = 2.01 \text{ \AA}$), $2a = 0.15^\circ$.

(d) Same as (c) but X-ray tube operated at 19 kV peak, 33 mA.

(e) Same as (c) but 0.0007" nickel filter placed between specimen and crystal.

(f) Same as (c) but pulse height analyzer set for W La and then for Nb Ka. The W La line is nearly but not completely eliminated.

aperture 0.58° , are shown in *fig. 19a*. The second order reflection of Nb Ka lies in the right hand side of the foot of the W La line, thus prohibiting a direct comparison of the relative line intensities of Nb and W.

If we increase the angular resolution of the instrument by reducing the aperture of the parallel slits to 0.15° , we obtain the line profile in *fig. 19b*. The second order Nb Ka line now shows as a slight hump on the lower right hand side of the WLa line, but the separation is still not complete.

If we now replace the quartz crystal with a LiF crystal, using the cleavage surface (200 plane, $d = 2.01 \text{ \AA}$), the larger angular dispersion separates the NbKa_1 lines in the second order from the WLa line, *fig. 19c*; relative intensity measurements can now be made with a fair accuracy although the overlapping is not yet completely eliminated.

Increasing the resolution and dispersion is a familiar expedient in optical spectrographic analysis, although larger instrumental efforts for its realization are required than in the X-ray method. The following methods of handling overlapping lines are unique for the X-ray case.

The excitation of the Nb K radiation can be avoided by lowering the X-ray tube voltage: the excitation potential of Nb Ka is approximately 19 kV, whereas the W La line appears at 10 kV. The effect is shown in *fig. 19d*. Owing to the full-wave rectified operation of the X-ray tube (cf. *fig. 10*) and its limited current capacity, the intensity of the W La line has been reduced by about a factor of 8 by the lowering of the voltage.

An overlapping line can in some cases be eliminated by using

a selective filter on the X-ray detector. This possibility is due to the fact that the absorption edges of elements are located at wavelengths which vary systematically with the atomic

Table IV. Sources of closely spaced spectral lines. Roman numeral indicates order of reflection.

Source	Lines	Wavelengths in Å
Elements close together in atomic number	{ 25 Mn Ka_1	2.103
	{ 24 Cr Ka_1	2.085
	{ 45 Rh La_1	4.374
	{ 46 Pd La_1	4.368
K-spectra of low atomic number overlap L-spectra of high atomic number	{ 30 Zn Ka_1	1.435
	{ 75 Re La_1	1.433
	{ 21 Sc Ka_1	2.780
	{ 56 Ba La_1	2.776
Higher orders of K-spectra of high atomic number overlap K-spectra of low atomic number	{ 28 Ni Ka_1	1.500 (I)
	{ 41 Nb Ka_1	1.494 (II)
	{ 42 Mo Ka_1	2.127 (III)
	{ 33 As Ka_1	2.114 (II)
Higher orders of K-spectra overlap L-spectra	{ 47 Ag Ka_1	1.677 (III)
	{ 70 Yb La_1	1.672 (I)
	{ 41 Nb Ka_1	1.494 (II)
	{ 74 W La_1	1.476 (I)

number, much in the same way as the emission lines. It is therefore possible in many cases to pick an element having an absorption edge which will affect one spectral line of the specimen much more than another line close to it. For the Nb + W sample, a nickel filter can be used: the nickel, having its K-absorption edge at 1.48 Å, selectively absorbs the W La radiation (≈ 1.43 Å) while hardly affecting the harder Nb K radiation. With a Ni-filter approximately 0.02 mm thick, the W La-line is almost completely eliminated, the NbK α lines being reduced in intensity by only a factor of about 2; see fig. 19e.

The final and most effective solution to the problem of overlapping lines is the pulse height discrimination technique. It is based on the fact that the pulse height generated in a proportional or scintillation counter by the absorbed X-ray quantum is proportional to the quantum energy, subject to a certain spread resulting in a finite "energy resolution" of the detector²³). Whenever the wavelength difference of two overlapping lines is larger than corresponds to this energy resolution, the lines can be separated by means of the electronic "window" of the pulse height analyzer. The two curves of fig. 19f illustrate this point: In the left curve the pulse height analyzer was set for the W La-radiation and it is seen that the W La $\alpha_1\alpha_2$ -lines are obtained while no Nb radiation is recorded; in the right curve the analyzer was set for the Nb K α radiation — only very little W La-radiation is recorded in this case. It should be noted that this method not only permits complete separation but also gives the highest intensities in both lines and is very easy to perform.

The three latter methods of handling overlapping lines — which were stated to be unique for the X-ray case — can effectively be applied to the case where the whole spectrum "overlaps", i.e., where the spectral lines are not dispersed by an analyzing crystal at all²⁴). Since the detector can be placed

very near to the specimen, the intensities are enormously greater than in the dispersive (diffraction) type of analysis, but on the other hand, it is not possible to eliminate scattered radiation so that the background of the measured intensities is relatively high. Non-dispersive analysis, therefore, is restricted to specimens with only a few constituents present in not too small concentrations.

Summary. In X-ray spectrochemical analysis, elements are identified and their concentrations determined by means of the wavelengths and intensities of lines in their characteristic X-ray spectra. This method, which in principle is similar to the well-known optical spectrochemical analysis, has several important advantages: It is non-destructive; it can readily be applied to all kinds of specimens, solid, powder or liquid, crystalline or amorphous; the X-ray spectra are very simple, cases of overlapping lines of different elements are not frequent, and a number of methods are available for separating or distinguishing them. The instruments developed for the method are simple to operate, so that it is quite possible that in the future X-ray spectrochemical analysis will be used for routine analytical work as extensively as the optical spectrochemical method.

The X-ray spectra are usually excited by way of fluorescence, induced by the continuous or characteristic radiation of an X-ray tube with tungsten or other target. A number of details concerning the primary target, the voltage and mode of operation of the X-ray tube and the nature of the fluorescing specimen are discussed in the article. The X-ray spectra are analyzed by diffraction from a single crystal; a Geiger counter, proportional counter or scintillation counter is used for measuring the reflected rays. The instrumentation thus is very similar to that used in X-ray diffractometry. A discussion of the X-ray optics for the fluorescence analysis and of the desirable characteristics of the analyzing crystal, the specimens and the standards used is also given.

The method is capable of good precision within reasonable time: quantitative analyses to within 1% or less can often be performed in a few minutes. Minor constituents down to 10^{-3} % or less have in some cases been determined. Specimens of a few milligrams can be handled when special focussing arrangements are used. The method is useful for all elements of atomic number between 13 (aluminum) and 92 (uranium); using a 50 kV X-ray tube, the K-radiation of elements 13 to 60 and the L-radiation of elements 34 to 92 can be excited. For the elements 13-24 the K-spectra lie between about 9 and 2.3 Å, and owing to the absorption in air, special techniques are required for these very soft X-rays.

²³) A. R. Lang, Wavelength resolution of X-ray proportional counters, *Proc. Phys. Soc.* **A65**, 372-373, 1952; C. F. Hendee and S. Fine, Moseley's law applied to proportional counter resolution of adjacent elements, *Phys. Rev.* **95**, 281-282, 1954 (1 July).

²⁴) See, for example, H. Friedman, L. S. Birks and E. J. Brooks, *Amer. Soc. Test. Materials, Spec. tech. Publ. No. 157*, Philadelphia 1954.

SERIES PRODUCTION OF CARRIER WAVE TELEPHONY EQUIPMENT



In the short-haul carrier telephony system STR 112, developed by Philips Telecommunication Industries at Hilversum*), an entirely new design is now used for the speech channel units. All the components and circuitry for each channel (including signalling circuits) are built into an airtight box (so-called "conclave" construction). This photograph shows the manufacture of these speech channel units on a moving belt. Along the belt (moving towards foreground of picture) the operations are, successively: wiring of the chassis, mounting of resistances and coils, adjustment of filters and coils and the assembly of the unit. In the middle foreground are four testing racks for measurements and adjustment of the units. At the end of the moving belt (foreground) are the high tension test rack and the final inspection.

*) Comm. News 14, 78-127, 1954, The photograph is taken from this publication.

A NEW FLUORESCENT LAMP IN A STARTERLESS CIRCUIT

by W. ELENBAAS and T. HEHENKAMP.

621.327.534.15

The fact that most tubular fluorescent lamps require a starter switch, and consequently flicker slightly during the starting period, is a disadvantage of these lamps, which otherwise offer important advantages. This objection is overcome in a new lamp ("TL" M lamp) and the associated ballast arrangement. Lamp and ballast are so designed that ignition is ensured even at low temperatures.

Introduction

In recent years there has been a general effort to go over to circuits for fluorescent lamps in which there is no need for a starter. This is a consequence of a desire for quicker and steadier ignition and, at the same time the elimination of a component that increases the risk of breakdowns. It is true that modern glow discharge starters are reliable and durable but, after all, their lifetime is not unlimited. Moreover it is not always easy, without measuring instruments, to find out whether a breakdown is due to the lamp or to the starter.

Even in the early years of the fluorescent lamp, attempts were being made to devise starterless circuits. Starterless outfits that were marketed at that time clearly possessed too many disadvantages, so they were adopted only on a limited scale and some of them disappeared soon afterwards. One example was the "Instant-Start" equipment, which was employed on a limited scale in America; this supplied a voltage of about 450 V for igniting the special "Instant-Start" 40 W lamps¹⁾. Here, the elimination of the starter brought with it the drawbacks that the ballast equipment had to be of greater size and higher price and caused bigger electrical losses, and that, since the lamp electrodes were not heated before ignition, electrodes of a special type had to be used.

Another example is the resonance device (fig. 1a) developed by Philips in 1939 for a 25 W lamp²⁾. On switching on, the electrodes are heated by a relatively high current and at the same time a voltage of about 350 V (r.m.s.) develops across the lamp, thus ensuring quick ignition. Here we shall give a brief explanation of the way the device works, in order to make clear the disadvantages of the circuit and the simplifications to it which will be discussed presently.

The circuit is to be regarded as a variant of the well-known Steinmetz circuit shown in fig. 1b. The self-inductance L_1 and the capacitance C_1 are in resonance at the frequency of the AC supply. For a supply voltage $E\sqrt{2} \sin \omega t$, the circuit has the following properties: the current through the impedance Z is $E/j\omega L_1$ and is therefore independent of Z ; if, moreover, the reactive part of Z is equal to ωL_1 , the input current is in phase with the supply voltage (power factor = 1). The first property has the consequence that, whenever the circuit is open at Z , the voltage across the break becomes very high. All this makes the circuit very attractive for employment with a fluorescent lamp, the lamp (in series with a choke coil) taking the place of the impedance Z .

In explaining the circuit of fig. 1a we may ignore the bimetal relay B , which will be dealt with presently, and likewise the capacitor C_2 , the sole purpose of which is to suppress radio interference.

On switching on, the position is as illustrated in fig. 1c. The electrodes are fed in series by a heating current I_h , which passes through the two coils S_1 and S_2 wound on the same core (each coil separately having the self-inductance L_2) in such a way that the resultant self-inductance is zero. Thus, if r represents the total resistance of the system and L_1 and C_1 are in resonance with the supply frequency, the current I_h is given by

$$I_h = \frac{E}{r}.$$

After ignition the position is that of fig. 1d. Connections may now be considered to have been made as indicated by dotted lines in the diagram, with the result that the circuit is transformed into that of fig. 1b; the lamp current I_{la} thus becomes

$$I_{la} = \frac{E}{j\omega L_1}.$$

¹⁾ R. N. Thayer and D. D. Hinman, Requirements for reliable instant-starting fluorescent lamps, *Illum. Eng.* **40**, 640-658, 1945.

²⁾ Netherlands patent No. 55 200.

The circuit parameters are such that $|I_h| \gg |I_a|$ (for rapid heating of the electrodes)³⁾ and at the same time the voltage across the lamp is high (350 V). This results in quick and reliable ignition of the lamp.

On account of the war it was not until 1945 that the circuit of fig. 1a was adopted on a fairly large scale, but it was unable to maintain its position for more than a few years. Here too, large size and

contact of this relay, normally open, then short-circuits the choke coil L_1 , reducing the current to a low value once again.

Two trends are discernible in the recent development of the fluorescent lamp: one towards special electrodes that are not pre-heated, the other towards more normal electrodes that are. An example of the first type is the Philips "TL" S 40 W lamp⁴⁾, in which an incandescent lamp alone constitutes

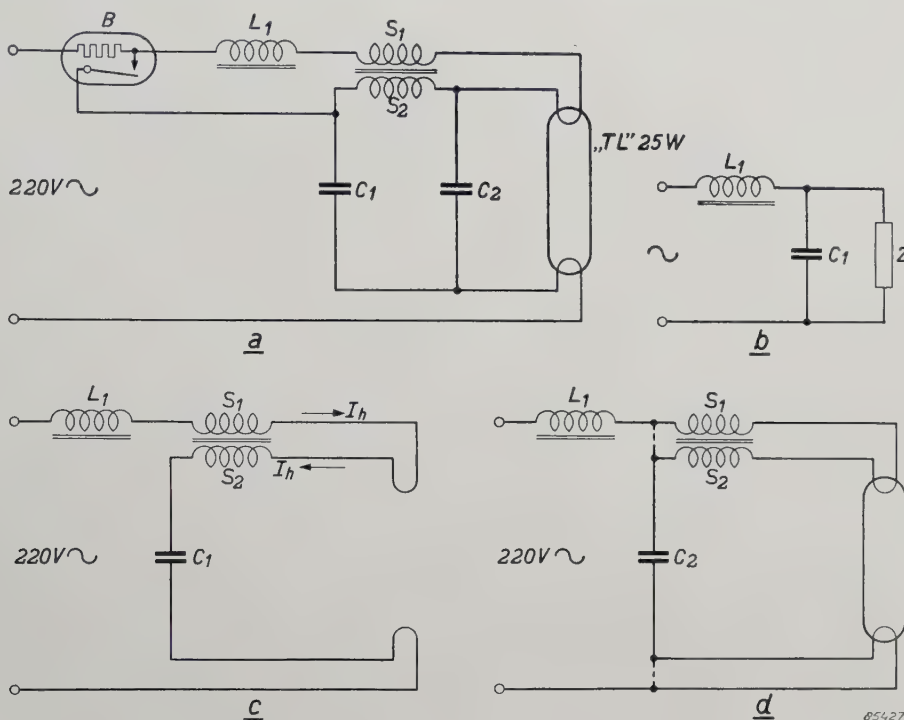


Fig. 1. a) Circuit diagram of a ballast for "TL" 25 W lamp, which was on the market in 1945. L_1 choke coil and C_1 capacitor slightly off resonance with the supply frequency. S_1/S_2 double choke. C_2 capacitor for interference suppression. B bimetal relay (excess current safety device). b) Steinmetz resonant circuit. With L_1 and C_1 in resonance with the supply frequency, the current through the impedance Z is independent of Z . c) Equivalent circuit of (a) before the lamp is ignited (B and C_2 omitted). The net self-inductance of S_1 and S_2 together is zero; there is a heavy heating current I_h flowing. d) Equivalent circuit of (a) when lamp is ignited. Connections may be considered to have been made along the dotted lines; the circuit is then effectively that of (b), in which Z represents the lamp in series with the shunt-connected chokes S_1 and S_2 .

high price were the objections and, these apart, the excess current safety device constituted a troublesome complication. This device was necessary because the state of resonance continued to exist when, at the end of the lamp's life, it failed to ignite; the heavy current I_h then persisting would have overloaded the equipment had it not brought the bimetal relay (B in fig. 1a) into operation. The

the whole of the ballast equipment. The second type has come to the fore in various countries^{5,6,7)} and is also represented in the new Philips "TL" M lamp, which will be discussed in this article. In both cases the ignition voltage of the lamp has been brought down by various means to a value considerably

³⁾ In general it is desirable to keep the resistance r low, with an eye to losses. However, since I_h would then take on excessively high values, it is necessary to deviate from resonance somewhat and thus to keep $|I_h| < |E/r|$ (but in any case $\gg |I_a|$). Out of resonance, I_a is no longer completely independent of Z ; nevertheless the reasoning remains valid in essentials.

⁴⁾ W. Elenbaas and T. Holmes, Philips tech. Rev. **12**, 129-135, 1950/'51.

⁵⁾ S. Anderson, Control gear for fluorescent lamps, G.E.C. Journ. **17**, 159-177, 1950.

⁶⁾ A. R. Lemmers and W. W. Brooks, New fluorescent lamp and ballast design for rapid starting, Illum. Eng. **47**, 589-594, 1952.

⁷⁾ J. Cates, Fluorescent discharge tube circuits and operating problems, Proc. Inst. El. Engrs., Part II, **100**, 389-400, 1953.

lower than in older types. This has not only opened the way for starterless circuits; it also has the consequence that the lamp is subjected to less damage when switched on.

Means of lowering the ignition voltage

It has long been known that the ignition voltage of fluorescent lamps can be considerably lowered by various means other than the pre-heating of the electrodes⁸⁾. Three methods have actually been adopted in practice:

- 1) a conductive strip or coating on the inside of the glass wall,
- 2) an earthed conductive strip on the outside of the glass wall, and
- 3) earthed metal surfaces in the immediate neighbourhood of the lamp.

The objection to the two last-named methods is that it is a condition for proper functioning that one of the lamp electrodes should have a sufficiently high potential difference with respect to the strip or plate. Now this is usually the case when the mains supply is earthed on one side, but not with non-earthed supplies nor with two phases of a three-phase supply earthed at the star-point. In method (3) this difficulty is sometimes overcome by applying a suitable potential to the metal plate via a resistor, instead of earthing it. This resistor must have a value so high that there is no danger when the plate is touched; this signifies, in accordance with the safety regulations in force in many countries, that the current through the body when contact is made may not exceed 0.5 mA. With one individual lamp it is easy to satisfy this regulation, but it becomes difficult when fittings are mounted in long rows: then the metal parts are interconnected so that the resistors lie in parallel, with the result that it could be dangerous to touch a fitting.

The "TL" M 40 W lamp

For the reason just mentioned, when a new lamp (the "TL" M) was developed the choice lay between an internal and an external strip (the latter connected via a resistor with one of the electrodes). The external strip was chosen, because this (unlike the internal strip) involved no extra energy loss (see the article cited in footnote⁴⁾, pp. 131-132). As we shall presently see, the highest voltage developing across the lamp is about 250 V, so that a resistance as low as 0.5 M Ω gives satisfactory protection against shock. A value of 1 M Ω has actually been chosen,

to keep well within the safety limit in all circumstances.

A well-known phenomenon in fluorescent lamps with external ignition aids is that the ignition voltage depends on the humidity of the air¹⁾. This is also the case to some extent in the lamp with an external strip connected via a resistor to one of the electrodes. In the "TL" M lamp, this phenomenon is completely eliminated by applying a silicone coating to the outside of the glass, which makes the lamp quite insensitive to humidity.

Choice of heating current and no-load voltage

In fig. 2 the ignition voltage of the "TL" M 40 W lamp is plotted against the heating current of the electrodes for various ambient temperatures. It is possible with the help of this figure to determine,

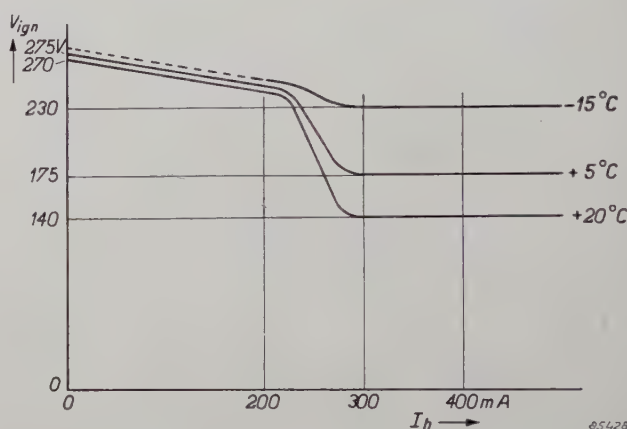


Fig. 2. Relation of ignition voltage V_{ign} of the "TL" M 40 W lamp to the electrode heating current I_h , for various ambient temperatures.

for a given electrode heating current, what no-load voltage is required from the ballast to give reliable ignition of the lamp in all circumstances. To this end, the curve is selected which relates to the lowest temperature to be expected in the field of application of the lamp; this curve is then corrected by a safety factor which allows for both the variations between one lamp and another and the deviations from the nominal supply voltage. The result is then as shown schematically in fig. 3. The region above curve 1 is that of reliable ignition.

In order now to narrow down the field of selection, regard must also be paid to other considerations. The most important criterion is the desired performance of the lamp under repeated switching conditions. This means the number of times that a lamp can be ignited before it fails, the burning time being extremely short. In normal practice a lamp will not be switched on more than a few

⁸⁾ W. Uytendhoeven, Elektrische Gasentladungen, J. Springer, Berlin 1938, pp. 92-93.

thousand times during its lifetime; however, the lifetime should not be limited by the criterion of the permissible number of switchings, so that several times this figure should be taken for testing purposes: 10 000 times, say, may be regarded as amply sufficient.

Extensive tests have made it clear that the no-load voltage has a big influence on the switching endurance, while the heating current has not, provided it remains above a certain minimum value. The result of these tests is also shown in fig. 3: the permissible region is that below curve 2. The hatched-in region between curves 1 and 2 is thus suitable for realising the aim in view.

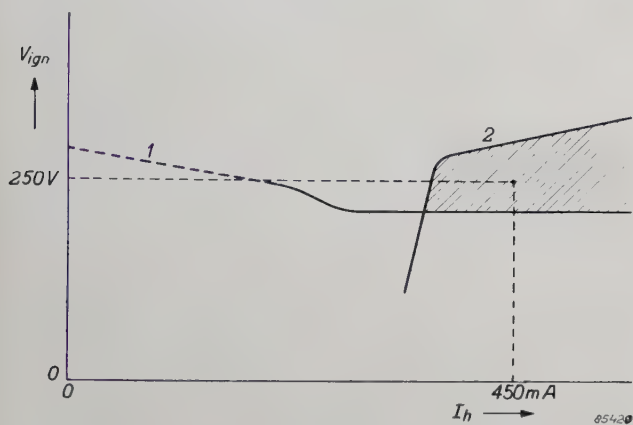


Fig. 3. Curve 1: V_{ign} as a function of I_h for the lowest ambient temperature at which the lamp must still ignite, modified by a safety factor which takes into account the spread between lamps and mains voltage fluctuations.

Curve 2: Limit below which the ignition voltage must be kept in order to obtain a sufficient switching endurance. The hatched in area represents the region of dependable ignition with high switching endurance.

In order that the ballast should have small dimensions it is generally desirable to choose the lowest permissible values for the heating current and no-load voltage. However, a higher heating current reduces the ignition time, so that in this connection a compromise must be sought. For the "TL" lamp the operating point indicated in fig. 3 has been chosen. It is clear that for this point the switching endurance goes well beyond the minimum requirement laid down, but after switching on some thousands of times a certain blackening was found to occur at the ends of the lamp. The fitting of shields around each electrode reduced this blackening effect to normal proportions.

Circuit for heating the electrodes

The current for heating the electrodes may be supplied in two basically different ways: maintaining a constant voltage or maintaining a constant current.

For constant voltage supply, the electrodes are

connected to secondary windings of a transformer which supply them with the correct filament voltage. With this method, the filament current is dependent on the resistance between each electrode and the transformer, in other words, on the leads and contact resistances in the lamp, lampholders and ballast⁹). It is above all the contact resistance in the lampholders which can be of importance, for it frequently occurs as a result of faulty installation (lampholders not properly spaced or angularly displaced with respect to each other) that one or more of the lamp pins make bad contact or none at all with the springs of the lampholders. One of the electrodes is then not heated, or not properly heated, and the consequences are once again blackening of the lamp ends and a sharp reduction in life. Another objection to constant voltage supply is that if a short-circuit occurs between the leads to the lampholder, the filament current transformer becomes overloaded — usually dangerously so.

For constant current supply, as is usual in circuits employing a starter, and also used in some starterless circuits adopted in the past (fig. 1a), the two filaments, in series with each other and with a high impedance, are connected to a source of fairly high voltage. The disadvantages referred to above are then absent: the current through the electrodes is practically independent of possible contact resistances, whilst if contact is broken altogether both electrodes remain dead; in such a case the lamp fails to start but is not exposed to damage.

The ballast equipment for the "TL" lamp

The foregoing will have made clear some of the important requirements to be satisfied by the ballast equipment for the "TL" lamp: at the time of ignition, a current of about 0.45 A must pass through the electrodes in series, while at the same time there must be a voltage of about 250 V across the lamp.

It was obviously worthwhile to investigate the extent to which the resonant circuit device (fig. 1a) could be adapted so as to satisfy these requirements. After all, the device combines several highly desirable properties: constant current filament supply, high power factor, little distortion of the current taken from the mains, and high impedance to frequencies which are adopted for AF control signals¹⁰) in mains supplies.

⁹) W. Calvin Gungle, Electrical characteristics of lamps and ballasts, *Illum. Eng.* **48**, 579-584, 1953.

¹⁰) This refers to techniques for the telemetering of information and for remote control via the mains.

A first simplification is that the fairly low heating current and the low ignition voltage of the “TL”M lamp make the excess current safety device superfluous; the bimetal relay can therefore be dispensed with. Further, the choke coil L_1 can be obviated by providing the double choke coil S_1/S_2 with a suitable leakage. The circuit diagram is thus simplified into that of *fig. 4*.

That the properties desired are actually obtained by the means outlined above may be demonstrated with the aid of the equivalent circuits in *fig. 5*, in which the values indicated for the various impedances are those selected for an equipment for a mains supply of 220 V at 50 c/s.

During the starting period the current taken from the mains, which serves to heat the electrodes, is determined by the leakage reactances and the capacitance (*fig. 5a*). This current amounts to $220/(640-80-80) = 0.45$ A. The voltage between

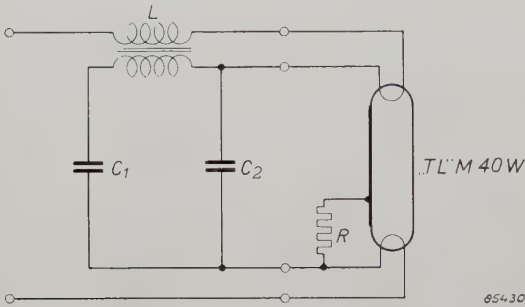


Fig. 4. Circuit diagram of ballast for “TL”M 40 W lamp. The two coils L on one core possess a certain leakage. C_1 resonance capacitor. C_2 capacitor for interference suppression. R resistor of 1 M Ω connecting the conductive strip to one of the electrodes.

the ends of the lamp is thus $0.45 \times (640-80) = 250$ V. Immediately the lamp ignites, the equivalent circuit of *fig. 5b* becomes applicable. It follows from the vector diagram (*fig. 6*) that the current taken from the mains is practically in phase with the mains voltage, so that the power factor is nearly 1. It may be seen from *fig. 5c* that the higher harmonics set up by the fluorescent lamp in the lamp current arrive at the mains much attenuated, for the circuit acts as a low-pass filter. The current taken from the mains is in consequence practically sinusoidal — an unusual property for a device with a high power factor. The impedance of the whole circuit to audio frequencies such as those used in mains networks for control signals is obviously high, as a consequence of the leakage reactances.

Performance in practice

Practical tests have been carried out on a large number of “TL”M lamps with their ballast equip-

ment in order to find out whether the results came up to expectations.

At 20 °C and the rated mains voltage, ignition is shown to take place evenly and without flickering in about 1.5 seconds. At lower temperatures and

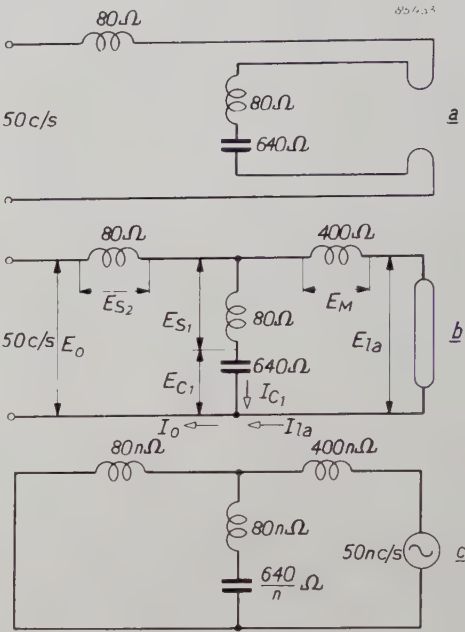


Fig. 5. Impedances occurring in the circuit of *fig. 4*:
a) before lamp ignites, frequency 50 c/s;
b) with lamp ignited, frequency 50 c/s;
c) with lamp ignited, frequency 50n c/s. Owing to the impedance of $80n\ \Omega$ in series with the supply, the mains current is distorted only very slightly.

mains voltages this time becomes only a little longer; down to $-15\ ^\circ\text{C}$, ignition is still reliable at 90% of the nominal supply voltage. The number of switchings before failure occurs amounts on the average to about 20 000. With 3 hours burning per start, which corresponds more to working conditions, the average lifetime is 7500 hours. The life of the lamp usually comes to an end as a result of one of the electrodes melting through; the flow of current through the equipment is thereby interrupted.

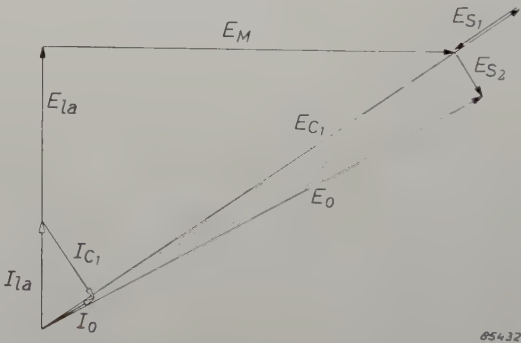


Fig. 6. Vector diagram relating to *fig. 5b* (see this figure for the meaning of the symbols).

The "TL" S 40 W lamp with the ballast equipment of the "TL" M lamp

We should like to mention in conclusion that the ballast equipment described above is also very well suited to the "TL" S 40 W lamp. For this lamp, in series with the associated incandescent lamp as ballast resistor, a mains voltage of 220 V is sufficient for ignition. On the other hand, if a ballast choke coil is employed, a higher voltage is necessary. The reason for this is that the low resistance of the incandescent lamp in the cold state allows a higher glow-discharge current to pass through the "TL" S lamp than does the high impedance of the choke coil; this heavier glow-discharge current helps towards ignition⁴). As we saw above, the ballast of the "TL" M lamp supplies a no-load voltage of 250 V, and this proves to be sufficient to ignite the "TL" S lamp at ambient temperatures not lower than 5 °C. Since the "TL" S lamp requires no heating current, it is possible to reduce the size of the equipment somewhat and also the number of terminals; a special version for the "TL" S lamp originated in this way.

Comparing the "TL" S with the "TL" M lamp, the former is found to ignite more quickly — almost

immediately after switching on in fact. Against this, the "TL" M lamp continues to ignite at ambient temperatures as low as -15 °C, exhibits a greater switching endurance and, since the internal strip of the "TL" S lamp is lacking, has a rather higher light efficiency.

Summary. The "TL" M 40 W lamp is a new tubular fluorescent lamp which functions without a starter. The ignition voltage lies below 250 V (r.m.s.) owing to two features: heating of the electrodes when the lamp is switched on and the presence of a conductive strip on the outside of the glass. The strip is connected to one of the electrodes via a 1 MΩ resistor. The ignition voltage is made independent of the humidity of the air by covering the lamp with a silicone layer. The ballast equipment is a simplified version of a device that was on the market in 1945. It is based on a Steinmetz resonance circuit. On switching on, it supplies a filament current of about 0.45 A to the series-connected electrodes, while simultaneously a voltage of approximately 250 V develops between them. The current taken from the mains is distorted only very slightly, the power factor is nearly 1 and the input impedance for audio-frequencies is high. At an ambient temperature of 20 °C and the rated mains voltage, the lamp ignites without flickering in about 1.5 seconds. At -15 °C ignition is still reliable at 90% of the rated supply voltage. The switching endurance amounts on the average to about 20 000 times. Allowing 3 hours burning for each time the lamp is switched on, the average lifetime is 7500 hours. Protection against excess current is not necessary.

A similar, somewhat smaller, ballast equipment has been developed for the "TL" S 40 W lamp, which was originally designed to operate in series with an incandescent lamp.

GROWTH SUBSTANCES IN PLANTS

by R. van der VEEN.

581.143:631.811.98

Growth substances are compounds of a hormonal nature which, although present in the plant in extremely low concentrations, govern the life of the plant. Much regarding these substances is still obscure. Until recently it was thought that the chemical structure of all compounds with growth substance activity (both natural and synthetic) conformed to two essential requirements, but the members of a newly discovered group of compounds appear to be active as growth substances, yet do not comply with these requirements. Paradoxically enough, in certain concentrations growth substances are lethal to some plants. This has found practical application in the control of weeds.

The concept of "growth substances" is intimately associated with the name of F. W. Went, who in 1926 while working in the Botanical Laboratory at Utrecht, discovered that the elongation of the stems of young plants was essentially caused by one specific substance.

It soon became apparent that this growth substance brought about many other reactions in the plant. A survey of the phenomena induced by growth substance is given below.

2. *Geotropism*. Growth substance is transported in a vertical downwards direction by the living cells. If a plant be placed at an oblique angle or horizontal, its lower side will receive more growth substance than its upper side. Consequently its lower side will elongate more, as a result of which the plant will again begin to grow upwards (*fig. 1a*).

The roots of a plant are even more sensitive to growth substance than its aerial parts. If a tap

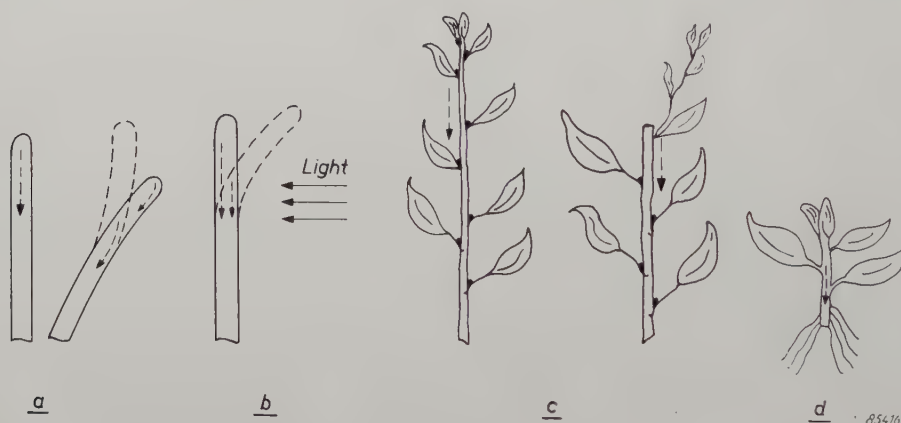


Fig. 1. a) *Geotropism*. In a stem set at an oblique angle, the lower side receives more growth substance than the upper side. The lower side thus grows more rapidly, and the stem curves towards the vertical.

b) *Phototropism*. On the lighted side of the stem there is less growth substance than on the shaded side; consequently the latter grows more rapidly, and the stem bends towards the light.

c) *Apical dominance*. Left: growth substance from the apex inhibits the development of the lateral buds. Right: on removal of the apex, the uppermost lateral buds sprout.

d) *Root formation*. The accumulation of growth substance in the lower extremity of a tap root brings about the development of roots.

In the figures, the dotted arrows indicate the movement of growth substance.

Reactions brought about by growth substance

1. *Elongation*. The cell walls of young cells elongate, often to many times their original length, under the influence of very low concentrations of growth substance. Greater concentrations of growth substance, however, inhibit this elongation.

root be laid horizontally, then here also more growth substance will be present on its lower side. This will lead to too high a concentration for the root growth, however, so that the elongation is not promoted, but inhibited, in such a way that the lower side grows slower than the

upper side, and the root will thus grow downwards.

3. *Phototropism*. It appears that growth substance is broken down by enzymes in the plant, and that the breakdown is powerfully stimulated by light. On the lighted side, therefore, the breakdown will be far more rapid than on the shaded side. In consequence the shaded side of the stem will grow more quickly, causing the plant to bend towards the light (fig. 1b). (This representation, though broadly accurate, is somewhat over-simplified).
4. *Apical dominance*. Much growth substance is formed in the rapidly growing apex of a plant. This growth substance is continuously transported down the stem. Now in each leaf axil is a lateral bud which can grow out into a lateral branch. Growth substance prevents the lateral buds from sprouting; in the presence of growth substance the buds thus remain dormant. If, however, the stem is decapitated (i.e. if its apex is cut off), the flow of growth substance is interrupted, and the lateral buds are thus able to sprout ¹⁾. The uppermost lateral buds sprout first (fig. 1c). Since the latter themselves produce growth substances the lower buds are arrested in their development and remain dormant.
5. *Root formation*. It has been found that a high concentration of growth substance stimulates the formation of roots. When a cutting is planted all the growth substance present in it, will be transported downwards and will collect in the lower end. For this reason the roots will form at that end and not higher on the cutting. By applying artificial growth substance to cuttings, the rooting process can be accelerated.
6. *Abscission*. The spontaneous shedding of leaves and fruits is usually caused by a reduction of the growth substance concentration in the plants, and can be readily prevented by the application of artificial growth substance to the plants, e.g. by spraying.
7. *The withering of certain blooms*. Many orchids, such as the popular Cattleyas, will often retain their freshness for more than 14 days on the plant. If they are pollinated, however, they wither in one day. Immediately after pollination, a large amount of growth substance is formed. The same effect is obtained by applying a little growth substance to the stigma, instead of pollen.

It is possible to go on enumerating phenomena induced by growth substance, but the above will suffice to give an impression of the highly important and varied role played by the growth substance in the life of plants.

Growth substances as weed-killers

As a consequence of its powerful hormonal nature, growth substance can ultimately give rise to a profound disturbance of various physiological equilibria in the plant, unless it is broken down in the latter. This disturbance may even be severe enough to bring about the death of the plant within one or two weeks, and has led to the practical application of synthetic growth substances as weed-killers (herbicides). Growth substances for use in this role must be very active and must not be rendered innocuous by the plant. Since the monocotyledons such as grasses and cereals are far less sensitive to growth substances than the dicotyledons, dicotyledonous weeds in grass and cereal fields can be eradicated by spraying with a specific amount of growth substance ²⁾. The best known of these so-called hormone weed-killers based on growth substance activity are 2,4-D[1] ³⁾, 2,4,5-T [2] and MCPA [3].

The chemical structure of growth substances

The chemical structure of the growth substance that plays the principle role in the plant kingdom is known. It is a compound of fairly simple structure and can be prepared synthetically, viz. 3-indolylacetic acid [4].

It is produced in the plant by the breakdown (in several steps) of the amino acid tryptophane, and is itself broken down further in turn, especially under the influence of light (see above). Indolylacetic acid is a link in a relatively long degradation chain. The concentration of the growth substance in a plant depends upon the rates of the various reactions in this chain. Since the indolylacetic acid breakdown reaction is dependent upon the illumination, a low light intensity will cause the concentration to be high and consequently the plant will proceed to elongate rapidly.

Following the discovery of the natural growth substance, numerous synthetic substances have been found that have a more or less analogous influence on the plant. Their number runs into hundreds. Some of them have but a weak growth substance action, others an action scarcely exceeded

¹⁾ For the correlation between this phenomenon and the length of day see R. van der Veen, Philips tech. Rev. **14**, 179, 1952/53.

²⁾ This possibility has already been mentioned in this journal, see R. van der Veen, Philips tech. Rev. **16**, 356-357, 1954/55.

³⁾ The numbers in square brackets refer to the structural formulae in the appendix.

by that of the natural growth substance. Some of the better known are summarized in the appendix.

It is truly remarkable that so many compounds, at first sight so widely different, exert an analogous action on plants. Attempts to find some correlation between the structures of the various compounds has occupied many workers.

In 1938 Koepfli, Thimann and Went ⁴⁾ established that all substances with growth substance activity have the following characteristics in common:

- a) a molecule with a "nucleus" consisting of a ring system,
- b) at least one double bond in this ring,
- c) one side chain on the ring,
- d) a carboxyl group at the end of the side chain, and separated from the ring by at least one carbon atom, and
- e) a special spatial relationship between the ring and the carboxyl group.

In 1949 Veldstra and Booy ⁵⁾ reduced these five characteristics to two, namely the possession of

- a) a ring system displaying a high surface activity, and
- b) a group of acidic character, which, on adsorption of the molecule at an interface, can come to lie outside the plane of the ring.

At the last held botanical conference (Paris 1954) both these characteristics were re-confirmed; no single exception to the characteristics of Veldstra and Booy had yet been found among the great number of compounds with growth substance activity.

A new group of growth substances

Co-operation between Philips-Roxane and the Organo-Chemical Institute of the Dutch National Council for Industrial Research, T.N.O., has recently lead to the discovery of a new group of compounds of fairly high growth substance activity ⁶⁾. There is no ring system in these compounds however, so that they do not comply with condition a)

⁶⁾ This work was conducted under the direction of Dr. Van der Kerk in the Organic Chemistry Laboratory at Utrecht. The discovery was reported in: G. J. M. van der Kerk, M. H. van Raalte, A. Kaars Sijpesteijn and R. van der Veen, *Nature* **176**, 308-310, 13 Aug. 1955.

⁴⁾ *J. physiol. Chem.* **122**, 763-783, 1938.

⁵⁾ *Biochem. biophys. Acta* **3**, 278-312, 1949.



Fig. 2. The reaction of tomato plants to spraying with solutions of N,N-dimethylthiocarbamyl glycollic acid [5] (code name KD 31) of various concentrations. Photograph (a) was taken two days, photograph (b) ten days after spraying. Even after ten days the plants treated with 0.05% and 0.1% solutions have still not recovered.

laid down by Veldstra and Booy, and thus do not conform to their formulation of growth substance characteristics. Examples of the new growth substances are N,N-dimethylthiocarbamylglycollic acid [5] and N,N-dimethyl-S-carboxymethyl-dithiocarbamate [5a].

In this new group of growth substances there is an atomic grouping that may be regarded as an intermediate form between



in place of the ring.

It is known from organic chemistry, that in the second structure, with a double bond between N and C, the atoms lie preferentially in one plane, and that this plane structure is imparted to a greater or lesser degree to all the molecules in which this group occurs. The new growth substances, therefore, have in their molecules an atomic group of plane structure, which takes the place of the ring system of the previously known growth substances.

In addition to this plane atomic group, the molecule contains a side chain, that is attached to

the right-hand carbon atom (in the above formulae). The side chain conforms to condition (b) of Veldstra and Booy, i.e. it is acidic in character, and will lie out of the plane containing the flat atomic group when the molecule is adsorbed at an interface.

Regarding the side chain, the following can be noted. Whether or not a compound of the recently-discovered type is active, depends upon the structure of the side chain in a manner that is completely analogous to that found for the side chains of the 2,4-dichlorophenoxy group. Thus the side chain $-\text{O}-\text{CH}_2-\text{COOH}$ for example, occurring in N,N-dimethylthiocarbamylglycollic acid [5] is very active; the action of solutions with different concentrations of this compound on young tomato plants may be seen in *fig. 2a* and *b*. If the side chain in question is replaced by $-\text{S}-\text{CH}_2-\text{COOH}$, a barely less active compound is obtained, with regard to its effect on the plant within two days (*fig. 3a*). After a longer period, the plant recovers from the effects of a high concentration of the sulphur-bridged growth substance (*fig. 3b*) but not from the effects of the oxygen-bridged growth substance (*fig. 2b*). The same is found for 2,4-dichlorophenoxy-



Fig. 3. The reaction of tomato plants to spraying with solutions of N,N-dimethyl-S-carboxymethyl dithiocarbamate [5a] (code name KD 2) of various concentrations, (a) two days (b) ten days after spraying. After ten days all the plants have completely recovered.

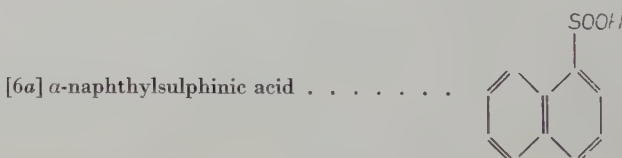
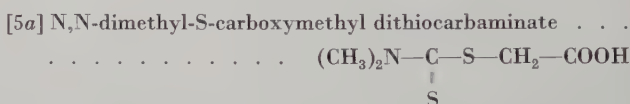
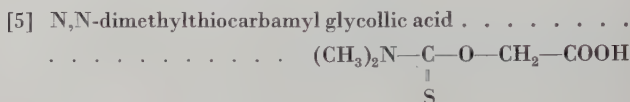
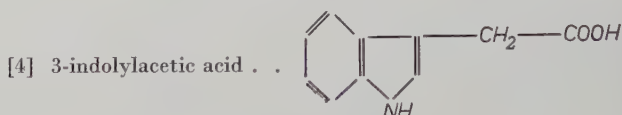
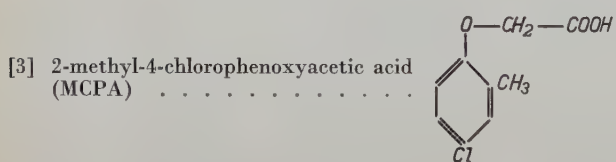
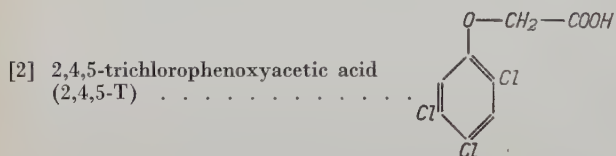
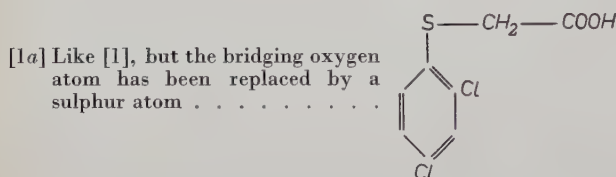
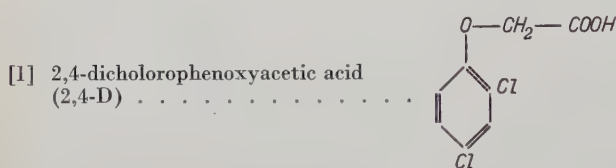
acetic acid (a growth substance of the old type having a ring system) if the bridging oxygen atom (cf. [1] and [1a]) in the side chain is replaced by a sulphur atom. Plants thus appear to be better able to break down a sulphur bridge than an oxygen bridge in this type of compound.

This is also illustrated by the following. α -naphthoic acid [6] displays growth substance action. On replacement of the carboxyl carbon of this acid by sulphur, α -naphthyl-sulphinic acid [6a] is formed; this compound is likewise active as a growth

substance, but is broken down very rapidly by the plant. Tomato plants, sprayed with an 0.1% solution, show a very pronounced reaction after one hour (consisting in a downward curving of the leaves) which reaches a maximum in eight hours. Recovery then sets in and after 24 hours there is no longer anything unusual to be seen. If the plants are sprayed with indolylacetic acid (the growth substance most widely occurring in nature), they also recover in the course of time, but the recovery is much slower.

APPENDIX: STRUCTURAL FORMULAE

Below are given the structural formulae of the compounds mentioned in the text.



Summary. After a survey of the principal reactions brought about by growth substances in plants, the use of growth substances in the combating of weeds is dealt with in brief. The author then passes on to the chemical structure of growth substances. The main growth substance is chemically fairly simple, viz. 3-indolylacetic acid, and can be prepared synthetically. The five common characteristics of substances with growth substance activity, framed by Koepfli, Thimann and Went in 1938, are then quoted. These were reduced to two in 1949 by

Veldstra and Booy. Philips-Roxane and the Organo-chemical Institute of the Dutch National Council for Industrial Research T.N.O., working in co-operation, however, have recently discovered a group of compounds of fairly high growth substance activity which have no ring system and do not therefore conform to the first condition of Veldstra and Booy. In the new group of growth substances, a similarly plane atomic group occurs in place of the ring system. A side chain attached to the atomic group does comply with the second condition of Veldstra and Booy.

A CINEMA PROJECTOR FOR 70 mm AND 35 mm FILMS

778.554.1

In the last few years various new systems of making and projecting films have been used. Philips is indirectly involved in one of these, viz. the Todd-A.O.¹⁾ system. The American Optical Company, the firm that undertook the development of the "Todd-A.O." system turned to Philips in Eindhoven for the development and manufacture of the necessary special projectors. We shall deal briefly with the "Todd-A.O. system" and its position in regard to two other well-known new systems, namely "Cinerama" and "CinemaScope", before turning to the projector itself.

The aim of these new systems is to strengthen the impression of "realness" created by the film. The method used in the above three systems is to photograph a wider field of view by using wide-angle taking lenses and to take up more of the field of vision of the audience with the projected picture by widening the screen. It is not sufficient to fill the bigger screen by projecting a normal film that has been enlarged still further; this would only produce the same effect as if the audience were to sit nearer to the screen.

It is most desirable to combine the use of a wide screen with stereophonic sound. The positions on the screen where the actions take place now vary so much that it would be distracting were the accompanying sound to come from just one fixed direction.

Increase in the picture angle at the filming stage has been taken furthest in the "Cinerama" system. In this system three cameras are used which take adjoining pictures, and this gives a total picture angle of 146° in filming. When these are projected, a wide curved screen is used on which the three films are projected next to each other (fig. 1) by three synchronized projectors. It is true, as can be seen from fig. 1, that the great majority of the audience will see the picture at an angle considerably less than 146° , but experience shows that this is not objectionable.

The success of "Cinerama", which in Europe has been seen in London, Paris, Milan and Rome, was so complete that audiences accepted the shortcomings of the system. From the audience's point of view the greatest objection is that the two dividing lines on the screen where the pictures join, have not yet been successfully eliminated. The brightness and colour of the three pictures are never absolutely alike. Moreover, every picture projected dances a little: the position of the frames on the film and the transport mechanisms of the projectors are never

quite perfect and this means that consecutive frames never occupy exactly the same position in the film gate. The dancing effect is not the same for each of the three films so that they can be seen to quiver with respect to each other at the picture boundaries. Possibly even more distracting is the fact that at a picture boundary the faults in the picture, though slight, change in a discontinuous manner. This can cause, for example, a long object situated across the width of the screen to show a kink at a picture boundary. This is especially annoying when an object of this kind (e.g. a boat)

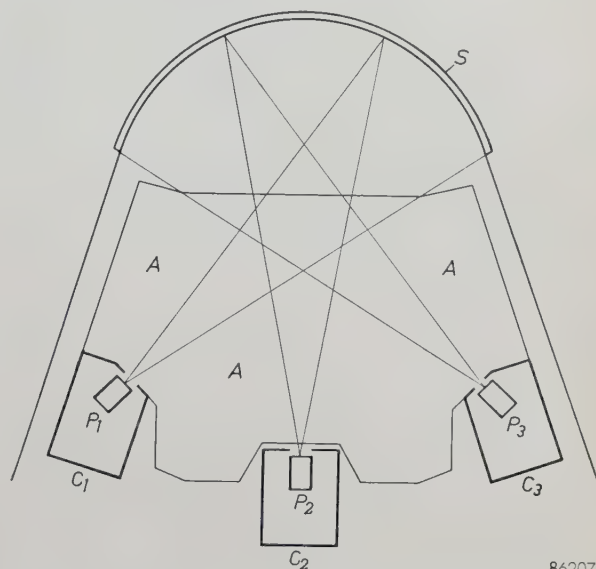


Fig. 1. Schematic diagram of the Cinerama system, showing the arrangement of the screen *S*, the three projectors *P*₁, *P*₂ and *P*₃ in their projection rooms *C*₁, *C*₂ and *C*₃, and the audience *A*.

moving right across the screen, passes a picture boundary.

From the point of view of the cinema management, "Cinerama" has the further disadvantage that the three projection rooms have to be placed in the auditorium itself, so that a considerable number of seats have to be given up to make room for them (fig. 1). Projection is not possible from rooms situated high up as the light beams would strike the screen obliquely and horizontal lines for instance would be reproduced as curved ones because of the curvature of the screen. Moreover, the whole arrangement is very complicated and several technicians are necessary to operate it. It is understandable that other systems have been tried with a view to achieving the desired effect while avoiding the difficulties mentioned.

An elegant approach to the problem was made possible by the development of a special wide angle

¹⁾ Todd is the name of the man who advocated the system; A.O. stands for "American Optical Company".

objective by Professor Brian O'Brien of the American Optical Company. This lens has a picture angle of 128° (but nevertheless has a comparatively large numerical aperture). A film taken with this lens consequently covers an area only slightly less than that of the three "Cinerama" cameras combined. Such a film can be projected on to a wide, curved screen and this produces, with a single projector, a similar effect to that of "Cinerama". Incidentally, the "picture angle" of the projector does not need to be made specially large.

This special objective forms the nucleus of the "Todd-A.O." system, but the system has other characteristic features. One of these is that it has completely broken with tradition by using 70 mm film in place of 35 mm and at the same time the frame frequency has been increased from 24 to 30 frames per second. The higher frame frequency produces smoother motion and lessens flickering in the picture reproduced on the screen. This is very desirable, for the eye is most sensitive to flickering at the periphery of the field of vision and, as a result, flickering on a wide screen might become noticeable.

The problem of obtaining a sufficiently bright picture on the large screen is greatly simplified by the wide film, since the area of the frame on 70 mm film can be made $3.5 \times$ as large as that on normal 35 mm. For the same luminous intensity on the film, 3.5 times as much light strikes the screen. In addition, the higher frame frequency contributes to less heating of the film.

Another important advantage is that the big screen can be filled without abnormally large magnification. With the small frame of 35 mm film, the grain of the film emulsion would be visible and would tend to blur the image.

In *fig. 2* we have a strip of 70 mm film and in *fig. 3* strips of normal 35 film and of 35 mm film for "CinemaScope". In all the films the perforations have the same spacing. With the 70 mm film, however, the height of the frame is 5 times the perfora-



Fig. 2. Strip of 70 mm film. It has six magnetic sound-tracks, three on either side of the film. The wide black bands on the outside of the perforations carry two sound-tracks each; the narrower bands inside the perforations carry only one each. The height of the frame is equal to 5 perforations.

tion spacing whereas it is only 4 times with 35 mm film; this means that the frame on the wide film is not only wider but also higher than that on normal film. In contrast with "CinemaScope", the scene is photographed on the film in natural proportions. The shape of the projected picture therefore corresponds to that of the frame (the film mask is 48.5 by 22 mm) and a so-called anamorphic projection lens (as in "CinemaScope") is not used.



Fig. 3. Strips of 35 mm film (a) normal and (b and c) "CinemaScope". The normal 35 mm film has one optical sound-track; the 35 mm "CinemaScope" film has either four magnetic sound-tracks, two on either side of the film (b), or one optical sound-track (c). Only in the second case (b) is stereophonic reproduction possible.

In "CinemaScope", for which many cinemas have already been adapted, 35 mm film is used. By means of the anamorphic lens used in this system, the picture is compressed in a horizontal sense (fig. 3*b* and *c*) when being taken. When the film is being projected the picture is expanded horizontally by a similar lens, so that the natural relationships are restored. The relationship of width to height of the projected picture can be larger by these means than it actually is on the film. The picture angle during shooting is about 90° as compared to 146° for "Cinerama" and 128° with "Todd-A.O."

On the wide film there is room for the six magnetic sound-tracks which give well-nigh perfect stereophonic reproduction. (A magnetic sound-track can give a higher quality of reproduction than an optical sound-track). Behind the screen there are five groups of loudspeakers, whilst in the auditorium there is a further number of loudspeakers used for special sound effects. Each group is supplied by its corresponding sound-track. It is now not necessary to have the six sound-tracks on a separate synchronously driven film as is the case with the "Cinerama" system. The greater frame-height and the higher frame-frequency combined, increase the film speed by a factor $\frac{5}{4} \times \frac{30}{24} =$ more than 1.5 times over that with normal film. This improves the quality of the sound: high frequencies can now be better recorded and reproduced.

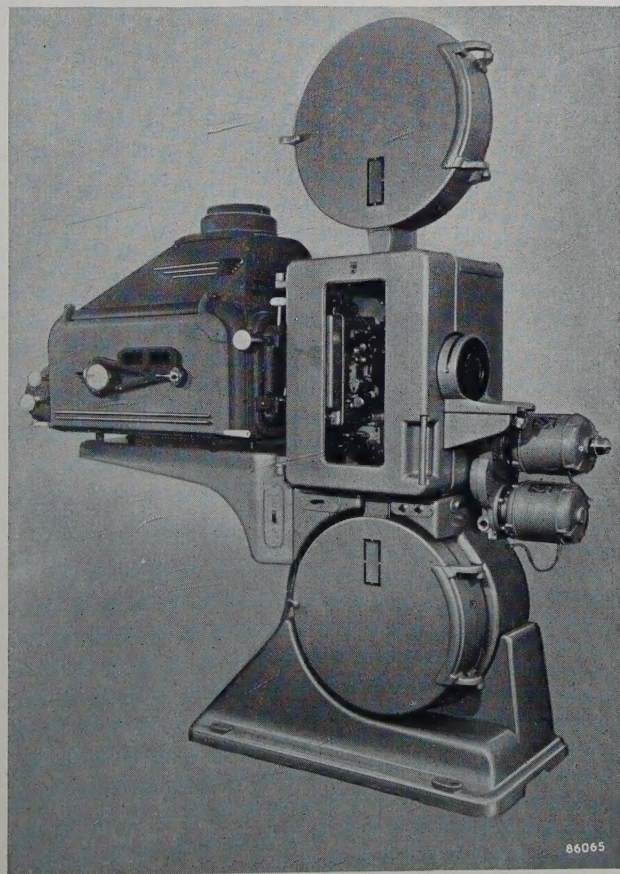


Fig. 4. The 70 mm film projector (type EL 4000) which at the same time is suitable for projecting normal 35 mm and "CinemaScope" films (with 4 magnetic sound-tracks or with one optical sound-track).

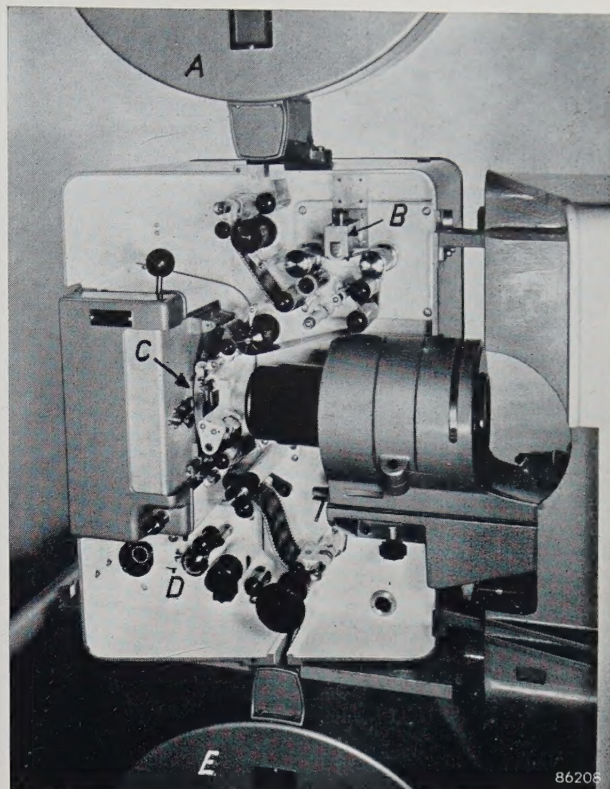


Fig. 5. Path of film when projecting either 70 mm or "CinemaScope" (35 mm) with magnetic sound-tracks. The projector in the figure is threaded with 70 mm film. After leaving the upper spool *A*, the film is fed past the magnetic sound head *B*. The film then passes to the take-up spool *E* via the curved film guide *C*, by-passing the optical sound head *D*. If normal 35 mm film or "CinemaScope" film with an optical sound-track is being projected, the film by-passes the magnetic sound head and is fed past the optical sound head.

The projector

As already mentioned, the special projector for the "Todd-A.O." system has been developed in Eindhoven and is now being manufactured there (Type EL 4000). The projector is so made that it is suitable not only for the new system but also for normal and for "CinemaScope" films. A cinema adapted for "Todd-A.O." is, with one type of projector, equipped for most other current projection systems at the same time (not, of course, for "Cinerama".) Fig. 4 is a photograph of the projector.

The projector has an optical sound head (for the optical sound-tracks on 35 mm film) and a magnetic sound head for 35 mm "CinemaScope" film and for 70 mm film. These heads are so arranged that the film can by-pass the heads not in use (fig. 5). The magnetic sound head has a total of 10 pick-ups (fig. 6); 6 of these correspond to the sound-tracks of 70 mm film and the other 4 to the sound-tracks on "CinemaScope" film (35 mm).

The sprockets have 4 toothed rims; the inner two are used for transporting 35 mm film, the outer

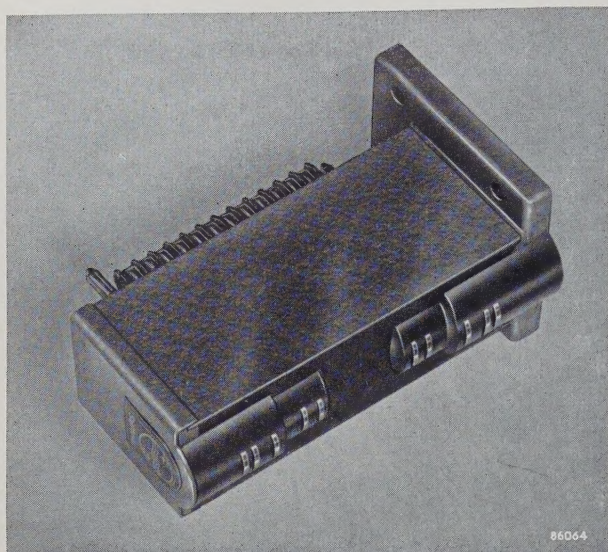


Fig. 6. The magnetic sound head of the EL 4000 cinema projector. 10 pick-ups can be seen as narrow ridges projecting from the mount. The four in the middle, which are those corresponding to the sound-tracks on "CinemaScope" film (35 mm), do not project quite as far as the others so that when 70 mm film is being projected they cannot cause any damage.

two for 70 mm film (fig. 7). The film is drawn forward by a 4-slot Maltese cross mechanism and the intermittent sprocket must therefore have a periphery equal to 4 times the size of the frame²⁾. As already stated, the height of the frame in 70 mm film is $\frac{5}{4}$ times that of 35 mm film. The periphery, and consequently also the diameter of the intermittent sprocket must differ by this same factor for the two sizes of film. Hence the 70 mm film is clear of the sprocket teeth for 35 mm film.

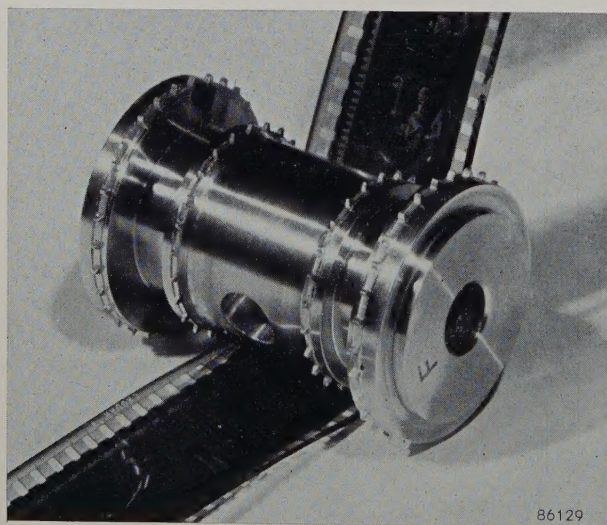


Fig. 7. Sprocket for 70 mm and 35 mm film. The toothed rims in the centre (for transporting 35 mm film) are set deeper so that they clear the 70 mm film.

The sprocket shown in fig. 7 is the type used both for the take-off sprocket and for the take-up sprocket, which respectively draw the film at uniform speed from the feed spool and lead it on to the take-up spool. The diameters of the toothed rims for 70 mm and 35 mm film also differ by a factor of $\frac{5}{4}$ but the peripheries are six times the size of the frame.

When transferring from one film size to the other, some re-adjustments have to be made: e.g. the film guide (which guides the film at the gate, see fig. 5) and the pad rollers (which keep the film on the teeth of the sprockets) have to be changed. In addition the speed of the projector has to be changed and for this purpose the apparatus has 2 motors (visible in fig. 4) and a selector switch. The objective too must of course be the correct one for the projection system in operation.

70 mm film has a greater tendency than 35 mm film to buckle in the film gate under the influence of the heat generated by the arc lamp. This would cause the projection to become blurred and so to prevent this, the film guide has been slightly curved (fig. 5) which gives the film more rigidity at that point. The normal flat pressure springs need now to be replaced by thin steel strips, whose tension can be adjusted and which press the film tightly to the gate.

The projector is fitted with a single-blade rotating shutter and the two interruptions per frame that are necessary are achieved by allowing the shutter to make two revolutions in this period. The effective region of the shutter blade is at the outer edge and at a large distance (about 12 cm) from the point of rotation. This blade interrupts the light-beam only 12 mm from the film at a point where the diameter of the beam is small. With these measures shutter losses are reduced to 46%³⁾.

The high number of revolutions of the shutter (3600 revs/min for 70 mm film) cause the projector to run with more noise than is usual. Also the flapping of the wide film is noisier than that of normal film. This is due to the increased width, the greater frame-shift and the higher frame-frequency. However, when the door of the projector is closed, the noise is not annoying for the operator.

The "Todd-A.O." system had its public debut on 13th October 1955 with the film "Oklahoma" shown in the Rivoli Theatre on Broadway, New York. The strip of 70 mm film reproduced in fig. 2 contains a scene from this film.

J. J. KOTTE.

²⁾ See Philips tech. Rev. 16, 158-171, 1954/55.

³⁾ The high speed of the effective part of the shutter blade produced by the doubled rotation speed and the large radius of the shutter, lessen the effect of the so-called "covering angle". A small beam diameter at the point of interception is also favourable in this connection. See article quoted in ²⁾.

ABSTRACTS OF RECENT SCIENTIFIC PUBLICATIONS BY THE STAFF OF N.V. PHILIPS' GLOEILAMPENFABRIEKEN

Reprints of these papers not marked with an asterisk * can be obtained free of charge upon application to Philips Electrical Ltd., Century House, Shaftesbury Avenue, London W.C. 2.

- 2227:** M. E. Wise: A quickly convergent expansion for cumulative hypergeometric probabilities, direct and inverse (*Biometrika* **41**, 317-329, 1954).

Sampling without replacement from finite populations is treated. If n units are taken from a population of N containing Nx defectives, we may want to know the probability P that (say) c defectives or less are found in the sample of N ; or, conversely, what is the value of x corresponding to given values of c and P . It was generally believed that these results were far more difficult to work out than for the corresponding problem with "infinite batches" in which we do not have to allow for the units removed in the sample as affecting the composition of the rest of the batch; this case only involves binomial probabilities, whilst the finite batch case involves hypergeometric ones. This paper derives simple but accurate approximations for these probabilities and for the inverse case. The mathematical method is an unusual one and is given in full, as it might be usable in quite different problems leading to hypergeometric series. Two numerical examples are given, in each of which, for given c , points in a P - x curve are calculated and compared with the corresponding exact values.

- 2228:** P. F. J. Bogers: Organische stoffen bij demineralisatie (*Water* **38**, 229-302, 1954). (Organic substances in demineralization; in Dutch).

Report of investigations into the poisoning of ion-exchange resins by organic substances present in water.

- 2229*:** J. Smit and H. P. J. Wijn: Physical properties of ferrites (*Advances in Electronics and Electron Physics* **6**, 69-136, 1954).

Survey of theory and experimental results concerning the properties of Ferroxcube, up to the end of 1953. See also *Philips tech. Rev.* **8**, 353-360, 1946; **9**, 185-190, 1947/48; **11**, 313-322, 1949/50; **13**, 181-193, 1951/52; **16**, 49-58, 1954/55; and these abstracts Nos. 2092 and 2109.

- 2230:** F. A. Kröger and H. J. G. Meyer: The edge emission of ZnS, CdS, and ZnO and its relation to the lattice vibrations of these solids (*Physica* **20**, 1149-1155, 1954).

It is shown that the vibrational structure appearing in the luminescent emission close to the fundamental absorption bands of ZnS, CdS and ZnO corresponds to the frequency of the longitudinal lattice vibrations of the optical branch. This proves that the edge emission is a property of the pure, unperturbed lattice. In connection with observations by Klick it is concluded that the fluorescence is due to excitons. The appearance of double peaks in the infra-red absorption spectrum of ZnO and BeO is explained by a two-phonon process, involving phonons of the optical and acoustical branch according to a theory given by Born and Blackman.

- 2231:** C. Z. van Doorn: Temperature dependence of the energy-gap in ZnS (*Physica* **20**, 1155-1156, 1954).

The temperature dependence of the energy-gap in ZnS was determined by direct measurement of the shift of the absorption-edge as a function of temperature. The results were in good agreement with calculations by W. W. Piper and measurements by J. H. Gisolf.

- 2232:** T. Tol: Fundamentale Probleme bei der Röntgen-Kinematographie mit Bildverstärker (*Research Film*, No. 5, pp. 1-6, Dec. 1954). (Fundamental problems in X-ray cinematography with the image intensifier; in German).

Brief survey of selected topics presented in previous article in *Philips tech. Rev.* **17**, 69-97, 1955/1956 (No. 3).

- 2233:** L. A. Æ. Sluyterman and H. J. Veenendaal: The rate of condensation of some tripeptide methyl esters in solution (*Rec. Trav. chim. Pays-Bas* **73**, 1001-1008, 1954).

The condensation rate of a few tripeptide methyl esters in methanol has been studied at 65 °C. The peptide esters with a glycyl residue at both ends have been found to be equally reactive, regardless of the nature of the amino acid residue in the middle. A side chain situated on one of the terminal amino acid residues decreases the reaction rate.

- 2234:** C. G. J. Jansen, R. Loosjes and K. Compaan: Distribution anormale des vitesses des électrons émis par une cathode à oxydesen, régime d'impulsions (*Le Vide* **9**, 129-134 1954).

French version of paper published in Philips Res. Rep. 9, 241-258, 1954 (see these abstracts No. R246).

2235: C. G. J. Jansen, R. Loosjes, J. J. Zaalberg van Zelst and G. A. Elings: Une méthode oscillographique pour déterminer le Potential d'Extraction en fonction de la température (Le Vide 9, 135-138, 1954).

An oscillograph has been developed which describes the saturation emission current i_s of a diode as a function of the temperature T of the cathode. The curve is described in about ten seconds, during which the anode-cathode voltage remains practically constant. The temperature T is measured by a Pt-PtRh thermocouple connected to the metal of the indirectly heated cathode. As the $i_s = f(T)$ curve is determined in such a short time, the effects of poisoning of the cathode surface are kept to a minimum. Moreover, it is possible to determine very quickly not only the work function ϕ of the cathode but also its temperature coefficient $d\phi/dT$ from a graph of saturation current density j_s as a function of absolute temperature, with the help of Richardson's formula.

2236: A. Venema: Applications de la cathode L (Le Vide 9, 269-272, 1954).

The construction and working of the L -cathode are described and some of the special precautions necessary in its fabrication are mentioned. The special properties of this type of cathode are then dealt with in connection with the metallic emitting surface (no oxides) and the replenishment of the activating material (barium). The application of the L -cathode in the EC56 disc-seal triode (power amplifier, up to about 4000 Mc/s) is described. Another example of its use is in the 4J50 magnetron, which gives a 250 kW output at a wavelength of 3 cm. The use of the L -cathode in klystrons and in X-ray tubes is also described.

2237: J. Meltzer: Morphological notes on Bryobia forms of fruit trees and ivy (Entomologische Berichten 15, 337-339, 1955).

Bryobia mites (*Bryobia praetiosa* Koch) found on apple and pear trees appear to differ morphologically and in size from those found on ivy. The author believes that the two types represent different species. There are indications that those living in

fruit trees cannot live in ivy, and vice versa. Owing to unfavourable weather, experiments to test this hypothesis have not given definite results.

2238: J. G. van Pelt and H. Keuker: De electro-metrische Karl Fischer titratie (Chem. Weekblad. 51, 97-99, 1955, No. 7). (The electro-metric Karl Fischer titration; In Dutch).

A simple and practical apparatus for electro-titration for the determination of water and a method for quick preparation of the necessary reagents.

2239: N. W. H. Addink, J. A. M. Dikhof, C. Schipper, A. Witmer and T. Groot: Quantitative spectrochemische Analyse mittels des Gleichstromkohlebogens (Spectrochimica Acta 7, 45-59, 1955, No. 1). (Quantitative spectrochemical analysis by means of the D.C. carbon arc; in German).

Detailed account of the "Constant Temperature Arc" method of analysis developed in Eindhoven (see N. H. W. Addink and W. de Groot, Philips tech. Rev. 12, 337-348, 1950/1951. The method consists of completely volatilizing 5 mg of a powdered sample in a shallow anodic crater of a carbon arc, with the addition of materials to modify the rate of volatilization if required. The line intensities are calibrated and corrections are made by comparison with selected Fe-lines, originating from a "standard light source" so as to get comparable analytical results; the calculations required are illustrated by several examples which also indicate the accuracy of the method. Tables are given of the empirically determined K-values, so that they can be checked in other laboratories.

2240: A. Kats and J. M. Stevels: Colour centres in alkali silicate glasses (Z. physik. Chem. 3, 255-260, 1955, No. 3-4).

It appears that the theory of colour centres, caused by X-ray and U.V. irradiation, as developed in recent years for alkali halides, also holds for alkali silicate glasses. The effect of such irradiation has been studied by the changes in the absorption spectrum between 2000 Å and 10 000 Å for various glasses with different alkali oxide content. The theoretical background of the results is briefly discussed; a full account of this work will appear in Philips Research Reports.